ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF SCIENCE AND TECHNOLOGY

GRAFTING OF POLY (2-(DIMETHYLAMINO) ETHYL METHACRYLATE) ONTO CROSSLINKED POLY(VINYL BENZYL CHLORIDE) RESIN FOR REMOVAL OF ACIDIC DYES

M.Sc. THESIS

Merve HAMAMCI

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İSTANBUL TEKNİK ÜNİVERSİTESİ ★ FEN BİLİMLERİ ENSTİTÜSÜ

POLİ (2-(DİMETİLAMİNO) ETİL METAKRİLAT'IN ÇAPRAZ BAĞLI POLİ (VİNİL BENZİL KLORÜR)'E AŞILANMASI VE ASİDİK BOYALARIN ATIK SUDAN GİDERİLMESİNDE KULLANIMI

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MAYIS 2014

Merve Hamamcı, a **M.Sc.** student of ITU **Graduate School of Scıence Engineering and Technology** student ID 5**09121019**, successfully defended the **thesis/dissertation** entitled "**GRAFTING OF POLY (2-(DIMETHYL METHACRYLATE) ONTO CROSSLINKED POLY(VINYL BENZYL CHLORIDE) RESIN FOR REMOVAL OF ACIDIC DYES**", which she prepared after fulfilling the requirements specified in the associated legislations, before the jury whose signatures are below.

Thesis Advisor :	**Prof. Dr. B. Filiz ŞENKAL** İstanbul Technical University	.....
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Date of Submission : 5 May 2014
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To my family,

FOREWORD

I would like to thank all people who made this work possible.

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May 2014

Merve HAMAMCI
Chemist

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ABBREVIATIONS

AIBN	**:** Azobisisobutyronitrile
ATRP	**:** Atom Transfer Radical Polymerization
CAC	**:** Activated Carbon
CRP	**:** Controlled Radical Polymerization
DMAEM	**:** 2-(dimethylamino) Ethyl Methacrylate
EDTA	**:** Ethylenediaminetetraacetic Acid
EGDMA	**:** Ethylene Glycole Dimethactrylate
GP	**:** Grafting Percentage
HCl	**:** Hydrochloric Acid
HMTETA	**:** 1,1,4,7,10,10 Hexamethyltriethylenetetramine
KOH	**:** Potassium Hydroxide
Me_6TREN	**:** Tris(2 (dimethylamino)ethyl)amine
NaOH	**:** Sodium Hydroxide
PMDETA	**:** N, N, N, N, N''-Pentamethyldiethylene Triamine
PVA	**:** Poly(vinyl alcohol)
PVBC	**:** Poly (vinyl benzyl chloride)
SI-ATRP	**:** Surface-Initiated Atom Transfer Radical Polymerization
SiO_2	**:** Silicium Dioxide
VBC	**:** Vinyl Benzyl Chloride

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GRAFTING OF POLY (2-(DIMETHYLAMINO) ETHYL METHACRYLATE) ONTO CROSSLINKED POLY(VINYL BENZYL CHLORIDE) RESIN FOR REMOVAL OF ACIDIC DYES

SUMMARY

Dyes are important water pollutants which are generally present in the effluents of the textile, leather, paper, rubber, plastics, cosmetics, pharmaceuticals and foodstuff industries.

Dye wastewater discharge into environmental water bodies deteriorates the water quality, and may cause a significant impact on human health due to mutagenic, teratogenic or carcinogenic effects of some dyes or their metabolites

Synthetic porous polymeric sorbents (i.e., resins) are superb adsorbents for organic compounds and, because of their higher physicochemical stabilities and better regeneration properties, have been commercialized as alternatives to activated carbon for adsorption applications. Resin-based adsorption technologies have been successfully developed for removal of dyes from water.

In this study, two different sorbents were prepared. Crosslinked poly (2-(dimethylamino) ethyl methacrylate) Resin (Resin 1) was prepared starting from copolymerization of 2-(dimethylamino) ethyl methacrylate (DMAEM) and ethylene glycole dimethactrylate (EGDMA) (10%) by using suspension polymerization method.

Other core-shell type polymeric sorbent (Resin 2) was prepared according to the synthetic protocol:

1. Preparation of crosslinked poly (vinyl benzyl chloride) (PVBC)
2. Grafting of 2-(dimethylamino) ethyl methacrylate onto PVBC beads by using inverse atom transfer radical polymerization (ATRP).

The grafting percentage (GP) was determined by calculating the percentage increase in weight by using following equation:

$$GP = \left[\frac{(m_{gf} - m_0)}{m_0}\right] \times 100 \quad \textbf{(1)}$$

where, m_0 and m_{gf} are the weights of the beads before and after grafting, respectively and grafting degree was found as 46 %.

Polymeric sorbents were characterized by using analytical and spectroscopic methods.

Obtained polymeric sorbents were used to remove acidic dyes from water. In this study, Reactive Red, Everzol Black and Calcon were used as acidic dyes.

Dye sorption experiments were studied determination of dye sorption capacities depending on initial dye concentrations, pH and ionic strength.

According to the results, dye sorption capacities of the Resin 1 and Resin 2 were found as 0.57 and 0.90 g dye / g resin for Reactive Red respectively. Dye sorption capacity of resin 2 is higher than the resin 1. Because, grafting parts in the Resin 2 behaves like homopolymer.

Also, dye sorption kinetics of the resins were investigated. Kinetic models were applied for Resin 1 and Resin 2.

Three kinetic models were used to analyze adsorption kinetics at different initial dye concentrations, namely, pseudo-first-order, pseudo-second-order, and intra-particle diffusion models.

The Lagergren first-order rate equation is one of the most widely used equations for the sorption of solute from a liquid solution. For this model, the following relation was used for the variation of adsorbed concentration with respect to time.

$$log\left(\frac{q_{eq}}{q_{eq}-q_t}\right) = \frac{(k_1 \times t)}{2.303} \quad \textbf{(2)}$$

where k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) and q_{eq} and q_t denote the amounts of adsorption ($mg.g^{-1}$) at equilibrium and at time t, respectively. The slopes and intercepts of plots of log ($q_{eq} - q_t$) versus t were used to determine the pseudo-first-order rate constant k_1 and q_{eq}.

The kinetics of sorption are an important aspect of the process control of removal of pollutants. The linear form of the equation describing the adsorption kinetics by the pseudo-second-order model is as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_{e2}} + \frac{1}{q_{et}} \quad \textbf{(3)}$$

The rate parameters k_2 and q_e can be directly obtained from the intercept and slope of the plot of t/q_t versus t. If pseudo-second-order kinetics is applicable, the plot gives a linear relationship which allows computation of k_2.

If the results were investigated for resin 2, second order sorption kinetic model for Calcon and Rective Red and intraparticular model for Everzol Black are suitable. For resin 1, second order kinetic model for Reactive Red is suitable.

Dye sorbed resins were regenerated by using potassium hydroxide (KOH) solution in water-ethanol. Desorption capacity of the resin was found as 0.83 g dye/ g resin.

POLİ (2-(DİMETİLAMİNO) ETİL METAKRİLAT'IN ÇAPRAZ BAĞLI POLİ (VİNİL BENZİL KLORÜR)'E AŞILANMASI VE ASİDİK BOYALARIN ATIK SUDAN GİDERİLMESİNDE KULLANIMI

ÖZET

Boyalar, su kirliliğine sebep olan önemli maddelerdir ve genelde tekstil, deri, kağıt, plastik, kozmetik, ilaç ve gıda sektörlerinin atık sularında bulunmaktadırlar.

Boya atık suları çevresel sulara karışarak su kalitesini düşürür ve insan vücudunda insan sağlığını ciddi şekilde etkileyebilir. Bazı boyalar metabolizma üzerinde mutajenik, teratojenik, ya da kanserojen etki yaratabilir.

Çapraz bağlı polimer üzerine aşılanmış lineer polimerler, çözünürlüğü olmaması ve fonksiyonel grup bağlanabilme kolaylığı nedeniyle, çeşitli uygulamalar için bir potansiyele sahiptir. Birçok yüzey modifikasyon metodu geliştirilmesine rağmen, son yıllarda pratik uygulamalar için istenilen özelliklerin sağlanması amacıyla yüzey modifikasyonu sıklıkla kullanılmaktadır.

Gözenekli sentetik polimerik sorbentler (reçine gibi) organik bileşikler için mükemmel adsorbanlardır. Yüksek fizikokimyasal stabilitelerinden ve daha iyi rejenerasyon özelliğinden dolayı, polimerik sorbentler adsorpsiyon uygulalamalarında aktif karbona ticari bir alternatif olmuştur. Atık boyalı suların arıtılmasında reçine-bazlı adsorpsiyon teknolojileri başarılı bir şekilde geliştirilmiştir.

Atom Transfer Radikal Polimerizasyonu (ATRP) tekniği, başlatıcı fonksiyonu yüzey ile kovalent bağ yaptığı için, polimer zincirinin yüzeyden büyümesini sağlamaktadır.

Süspansiyon polimerizasyonunda başlatıcı, su ortamında dispers olmuş monomer fazında çözünebilmektedir. Genellikle, polimerizasyon serbest radikal polimerizasyonu ile ilerlemektedir. Dispers olan monomer fazının bozulmaması amacıyla küçük miktarda stabilizatör ortama katılmaktadır.

Bu çalışmada, iki farklı reçine hazırlanmıştır. 2-(dimetilamino) etil metakrilat (DMAEM) ve etilen glikol dimetakrilat'ın (EGDMA) (10%) süspansiyon polimerizasyon tekniği kullanarak kopolimerizasyonuyla, çapraz bağlı poli(2-(dimetilamino) etil metakrilat) (Reçine 1) elde edilmiştir.

Diğer 'core-shell' yapısındaki polimerik sorbent (Reçine 2) şu sentetik prokole göre hazırlanmıştır:

1. Çapraz bağlı poli(vinil benzil kolorür) (PVBC) sentezi.
2. Ters atom transfer radikal polimerizasyon tekniğini (ATRP) kullanarak PVBC taneleri üzerine 2-(dimetilamino) etil metakrilat aşılanması.

Aşılanma yüzdesi, ağırlık artışı kullanılarak şu eşitlik ile bulunmuştur:

$$GP = \left[\frac{(m_{gf} - m_0)}{m_0}\right] \times 100 \quad \textbf{(1)}$$

m_0 ve m_{gf} tanelerin aşılanma öncesi ve sonrası ağırlıklarıdır ve aşılama yüzdesi %46 olarak bulunmuştur.

Polimerik sorbentler analitik ve spektroskopik yöntemlerle karakterize edilmiştir.

Elde edilen polimerik sorbentler sudan asidik boyaların giderilmesinde kullanılmıştır. Bu çalışmada asidik boya olarak Reactive Red, Everzol Black ve Calcon kullanılmıştır.

Boya adsorblama denemeleri ile, başlangıç boya konsantrasyonları, pH ve iyonik etkinin değiştirilmesiyle, boya adsorplama kapasiteleri bulunmuştur.

Reactive Red için, Reçine 1 ve Reçine 2'nin boya adsorplama kapasiteleri 0.57 ve 0.90 olarak bulunmuştur. Reçine 2'nin boya adsorplama kapasitesini daha yüksek olduğu görülmektedir. Bunun nedeni, Reçine 2'nin aşılama nedeniyle homopolimer gibi davranmasıdır.

Ayrıca boya sorpsiyon kinetikleri de bulunmuştur. Kinetik modeller Reçine 1 ve Reçine 2 için uygulanmıştır.

Farklı başlangıç boya konsantrasyonlarında adsorpsiyon kinetikleri analizi için 3 kinetik model kullanılmıştır. Bunlar; 1. Derece, 2. Derece ve Molekül İçi Partiküler Difüzyon modelleridir.

Lagergren 1. Derece hız eşitliği, çözeltideki çözünenin sorpsiyonu için çok kullanılan eşitliklerden biridir. Bu modelde, adsorplanan konsantrasyonun zamana karşı varyasyonu ile şu ilişki kurulmuştur:

$$log\left(\frac{q_{eq}}{q_{eq} - q_t}\right) = \frac{(k_1 \times t)}{2.303} \quad \textbf{(2)}$$

Eşitlikte; k_1 1. Derece model için hız sabiti (min^{-1}), q_{eq} ve q_t dengedeki ve t zamanındaki adsorpsiyonun miktarını ($mg.g^{-1}$), t ise zamanı göstermektedir. $log(q_{eq} - q_t)$ - t grafiğinin eğim ve kayım değerleri, 1. Derece hız sabiti k_1 ve q_{eq} değerini vermektedir.

Sorpsiyon kinetikleri kirlilik arıtımı için önemli bir parametredir. Eşitliğin lineer formu, 2. Derece model adsorpsiyon kinetiğini açıklar:

$$\frac{t}{q_t} = \frac{1}{k_2 \times q_{e2}} + \frac{1}{q_{et}} \quad \textbf{(3)}$$

t/q_t – t grafiğinin eğim ve kayım değerlerinden, hız parametreleri olan k_2 ve q_e hesaplanabilir. 2. Derece model uygunsa, grafik lineerdir ve bu da k_2'nin hesaplanmasını olanak verir.

Reçine 2 için, ikinci derece sorpsiyon kinetiği Calcon ve Reactive Red boyaları için uygun iken; Everzol Black için intraparticle diffusion model uygun bulunmuştur. Reçine 1 için, Reactive Red boyası için ikinci derece sorpsiyon kinetiği uygundur.

Boya yüklü reçineler su-etanol çözeltisinde çözünmüş potasyum hidroksit (KOH) ile rejenere edilmiş ve reçinenin desorpsiyon kapasitesi 0.83 g boya/ g reçine olarak bulunmuştur. Desorpsiyon yüzdesi, oldukça iyi bir değer olan %94 olarak bulunmuştur.

1. INTRODUCTION

Linear polymers grafted onto crosslinked polymer resin offer numerous potential applications due to the combination of the non-solubility resin and the flexibility of the graft polymer side chains as the functional group carrier.

In recent years, surface modification has been of importance to provide chemicals with desired properties for practical applications, though many surface modification methods have been developed.

The atom transfer radical polymerization (ATRP) technique, for instance, provides chain growing mostly on the solid surface, provided that the initiator function is covalently bound to the surface.

The surface-initiated atom transfer radical polymerization (SI-ATRP) technique has attracted intensive interest for the surface grafting high density polymer brushes with controlled molecular weight, molecular weight distribution, and well-defined structure.

Another advantage of this method over common radical initiation methods is that only negligible homopolymer formation is observed when it is employed in graft copolymerizations. ATRP technique can be used even in heterogeneous conditions successfully and grafting from solid particles can be obtained with moderate or acceptable polydispersities. But more important is that, ATRP is expected to eliminate free polymer formation during the graft polymerization and provide a relatively easy pathway to core-shell type of polymers.

In the present work, poly (2-(dimethylamino) ethyl methacrylate) was grafted onto crosslinked poly (vinyl benzyl chloride) beads by using inverse ATRP method. The core-shell type resin was used to remove acidic dyes from water. Also, crosslinked poly (2-(dimethylamino) ethyl methacrylate-co-ethylene glycole dimethacrylate) resin was prepared and used to remove dyes and dye sorption capacities of the resins were compared and sorption experiment studies were performed. Also, experiments

were carried out at different pH and ionic strength. Kinetic studies and regeneration studies were also studied in this thesis.

2. THEORETICAL PART

2.1 Free Radical Polymerization

Free radical additon to alkenes is an essential reaction in organic and polymer synthesis [1,2]. In most cases this reaction is quite exothermic and rapid while with the loss of one π-bond, one σ-bond is formed. What makes the radical addition reaction an appealing synthetic pathway is that the fast rate of radical addition as well as its toleration to many functionalities. Hence, it has been extensively utilized for the synthesis of a variety of compounds ranging from complex natural products to good polymers.

At the same time, the radical addition reaction has fundemantal side reactions, specially, diffusion controlled radical-radical reactions through coupling or disproportionation (Figure 2.1). The radical addition reaction often becomes a non-exacting method to targeted products due to these side reactions are highly fast and unselective, they are hard to control. This difficulty is most expressed in the polymerization process, where the addition reaction must be repeated many times, and the accurate control of the reaction is even more critical. Regularly, the polymers gained from the radical process do not have well defined structures in terms of molecular weight, molecular weight distribution and functionalities. Thus the main challenge in polymer synthesis is that accurate control of radical polymerization [3].

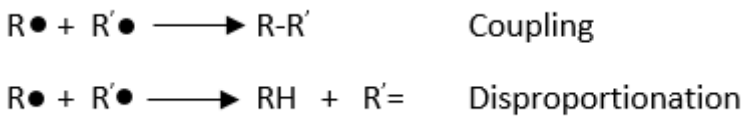


Figure 2.1 : Side reactions of radical additon reaction.

Luckily, the side reactions between radicals can be reduced by declining the radical concentration ([R*]). While radical - radical reactions are second order in [R*], the addition of radical to alkene is first order in [R*]. In addition rate the radical-radical

reaction effectively is suppressed by decreasing [R*] with a smaller reduction. There have been a number of useful methods to preserve low radical concentrations, mostly based on chain reactions in organic synthesis [1,2] (Figure 2.2). Exclusively a catalytic amount of radicals is commended since the radical is regenerated in the reaction cycle in the chain reactions.

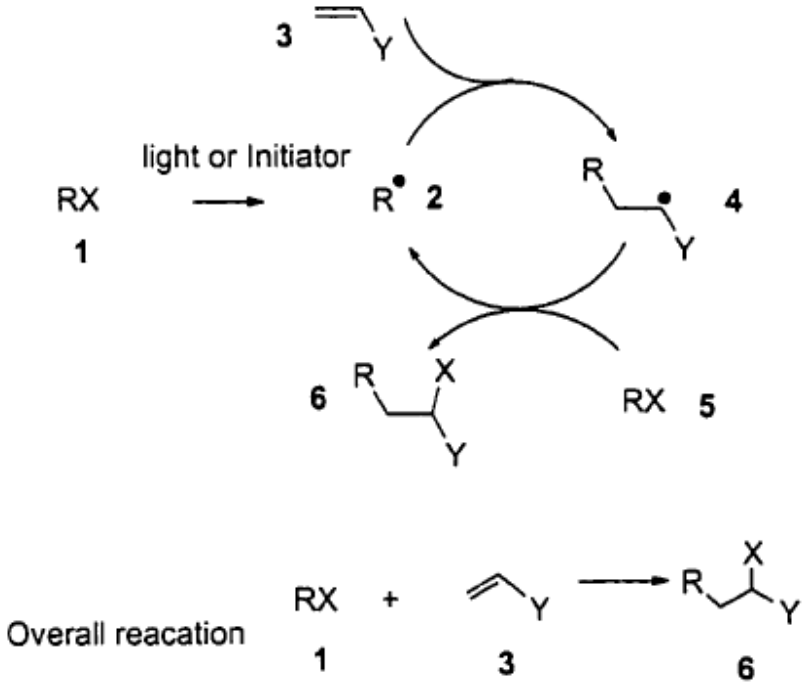


Figure 2.2 : An example of radical chain reactions [1,2].

2.1.1 Emulsion Polymerization

There are two immiscible liquid phases which an aqueous continuous phase and a non-aqueous discontinuous phase comprising of monomer and polymer in emulsion polymerization. The aqueous phase has initiator and the monomer-polymer particles are very small. Their size is 0.1 μm in diameter.

Higher-molecular-weight polymer can be assembled at higher rates with emulsion systems compare with bulk or suspension systems. The soap acts a signaficant role in emulsion polymerization. It exists in the form of micelles at the beginning of the reaction, combines of 50-100 soap molecules.

Most of the monomers stay as droplets a micrometer or more in diameter, some of the monomer passes into the micelles. In the ideal case no polymer is produced in the monomer droplets. In the lack of soap polymerization can occur (at a very low rate)

in the homogeneous phase, but this can not account for the bulk of the polymer formed polymer is formed in the soap micelles at the beginning of the reaction, these represent a favorable conditons for the free radicals generated in the aqueous phase, because of the connected abundance of monomer and the high surface / volume ratio of the micelles corraleted to the monomer droplets. The micelles grow by the addition of monomer from the aqueous phase (and ultimately from the monomer droplets) while polymer is occurred (Figure 2.3).

Soon the polymer particles much wider than the original micelles and absorb nearly all the soap from the aqueous phase. Any micelles not already activated disappear; further polymerization takes place within the polymer particles already formed. At this stage the monomer droplets are unstable; they blend into a continuous oil phase containing no polymer if agitation is stopped. The droplets act as reservoirs of monomer, which is fed to the growing polymer particles by diffusion through the aqueous phase. The rate of polymerization is constant over most of the reaction up to this point, but then falls off as monomer is consumed in the polymer particles. Soap (and initial micelle) concentration is increased by the rate [4-6].

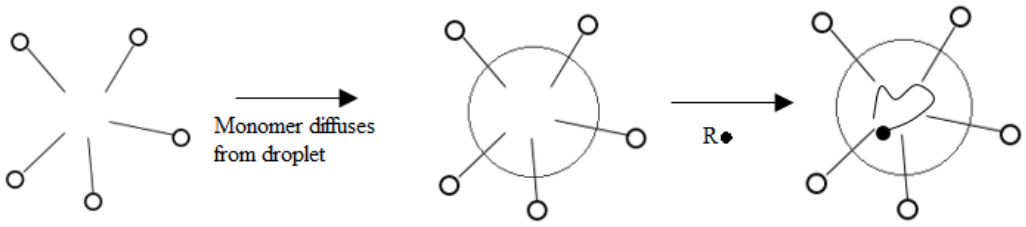


Figure 2.3 : Scheme of emulsion polymerization.

Advantages and disadvantages of emulsion polymers are demonstrated in Table 2.1.

Table 2.1: Common properties of emulsion polymerization [7].

Common Emulsion Polymers	Advantages	Disadvantages
styrene + copolymers vinyl chlorides ex. Pleather butadiene vinylidene chloride vinyl acetate vinyl acrylates (acrylics) methyl acrylates	low η (viscosity) great T control final product → fine powder or water form → coatings	a lot of soap as impurity ex. In medical applications, can be irritant

2.1.2 Suspension Polymerization

Suspension polymerization was devoloped first by Hoffman and Delbruch in 1909. The initiator is soluble in the monomer phase, which is dispersed by grinding into the dispersion medium (usually water) to form droplets in suspension polymerization. Dispersed monomer (droplet) phase and also the resultant polymer in the dispersion medium have usually low solubility. In most cases polymerization occurs by a free radical mechanism and continues in the droplet phase. Small amount of a stabilizer is required in suspension polymerization to hinder conglutination and break-up of droplets during polymerization. The size distribution of the initial emulsion droplets and, hence, also of the polymer beads that are formed, is dependent upon the balance between droplet break-up and droplet conglutination. The size distribution controlled by the type and speed of mixer used the volume fraction of the monomer phase, and the type and concentration of stabilizer used. At high conversion a gel is formed within the droplets at low conversion leading to harder drops if the polymer is soluble in the monomer. Precipitation will occur within the droplets if the polymer is insoluble in the monomer solution and the result in the formation of opaque, often irregularly shaped particles. If the polymer is partially soluble in the monomer mixture, the composition of the final product can be difficult to predict. Polymer beads are used wide range of appilacations such as molding plastics. However, their largest application is in chromatographic separation media (as ion exchange resin and as supports for enzyme immobilization). In the bead structure must have pores due to use some applications.

The addition of an inert diluent (or porogen) to the monomer phase which may be extracted after polymerization make the polymer beads porous material. UV stabilizers (aromatic ketones and esters), heat stabilizers (ethylene oxide derivatives and inorganic metal salts), molding lubricants and foaming agents (porogens) can be added to the monomer phase too [4-6].

2.1.2.1 Polymeric stabilizers

Poly (vinyl alcohol) (Figure 2.4), poly (vinyl-pyrrolidone), salts of acrylic acid polymers, cellulose ethers and natural gums are used for polymeric stabilizers in suspension polymerization. Batch reactor is used for suspension polymerization (Figure2.5).

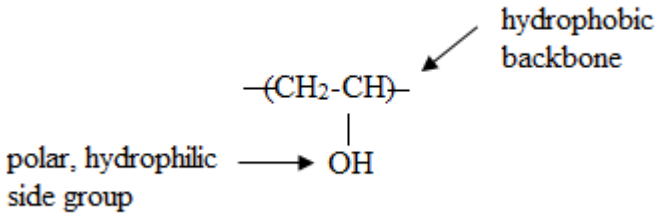


Figure 2.4 : Stabilizer for suspension polymerization (poly (vinyl alcohol)).

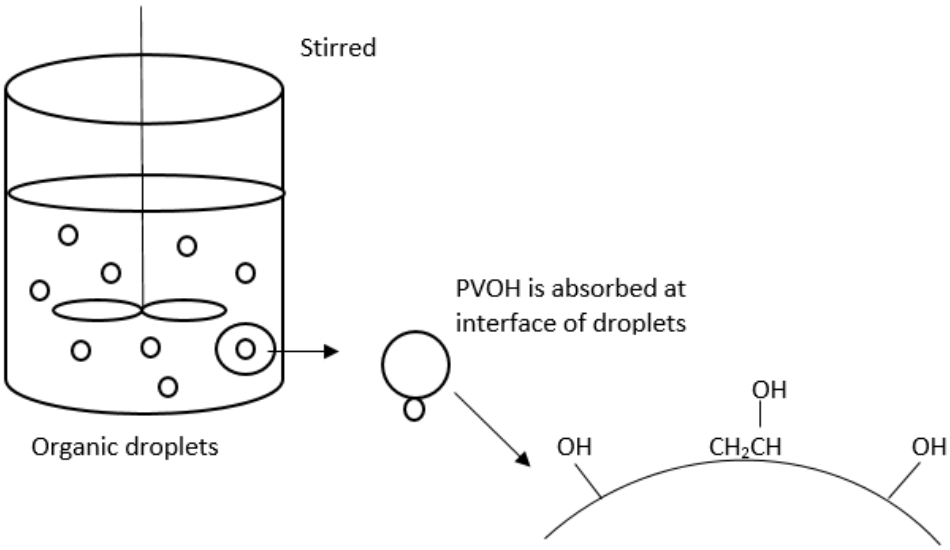
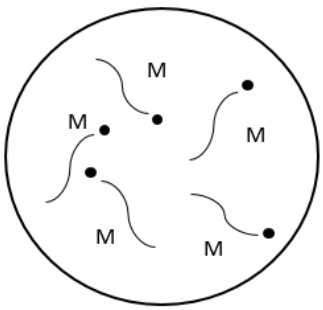


Figure 2.5 : Batch reactor within organic droplets (~1 μm – 1 cm).



Concerned with avoiding drop coalescence

- premix initiator + monomer
- agitate H_2O phase + add organic phase
-adjust impellar speed to get desired drop size
- add stabilizer (PVOH)
- continue stirring at more gentle speed and increase T to 40°C → 80°C depending on initiator type
- activation of initiator
- achieving close complete conversion

Figure 2.6 : Suspension polymerization.

2.1.2.2 Products

- Glassy rigid beads often called “latex beads”
- Very uniform
- Nice spherical shapes

2.1.3 Differences Between Suspension and Emulsion Polymerization

Table 2.2 Differences between suspension and emulsion polymerization

	Emulsion Polymerization	**Suspension Polymerizaton**
Composition	Monomer+Initiator+H_2O +Emulsifier	Monomer+Initiator+H_2O+Suspending Agent
Initiator	Soluble in H_2O	Soluble in monomer
Product	Latex	Suspended droplets
Product Size	0.05-5 μm	0.01-0.5 cm

2.2 Controlled-Living Radical Polymerization

We can refrain from chain termination step with two ways in controlled-living radical polymerization. These are increasing rate of initiation with respect to the rate of propagation or getting rid of chain termination and transfer reactions. Every chain length is approximately same and polymer chains grow at a more constant rate. These conditions can provide many types of reactions, e.g., atom transfer, nitroxide mediated.

Characteristics:

- Unless all monomers have consumed, the reaction continues. Polymerization resumes by adding monomer.
- Instead of Ri<<Rp in where conventional free-radical polymerization, in living polymerization $R_i > R_p$ (R_i and R_p are the rate of initiation and propagation).
- Between a propagating radical and dormant species dynamic equilibrium occurs.

- Opportunity of mono and/or narrow dispersities of the products.
- Molar mass of the grafted/crosslinked polymer molecules can be predicted.
- Usage of accurate terminating reagents can allow to synthesize telechelic polymers.

2.2.1 Atom Transfer Radical Polymerization (ATRP)

Atom Transfer Radical Polymerization (ATRP) is a type of controlled radical polymerization (CRP) technique which is the most powerful and versatile method [8–12]. M_w, M_{wd}, and functionality can be controlled accurately [13] and it can be carried out in a range of different solvents and conditions even in water at room temparature. We can synthesize products including functional groups by ATRP. The reaction conditions and parameters can be adjusted, providing reaction kinetics. Polymers can be grown from surfaces, proteins, organic materials, and inorganic materials including nanoparticles, additively homogeneous and heterogeneous solution polymerization [14]. We can synthesize hydrogels with it in imaging, diagnostics and biosensors.

In 1995, ATRP was first announced in primary publications [8, 15]. In many fields of polymer science, it has powerfully affected, inspiring quite interest in living polymerizations. The basic characteristic of ATRP [8,9,15–20] is the equilibrium between a low concentration of active propagating species and a larger number of dormant chains, via an inner sphere electron transfer process encouraged by a transition metal complex (Figure 2.7) [21,22].

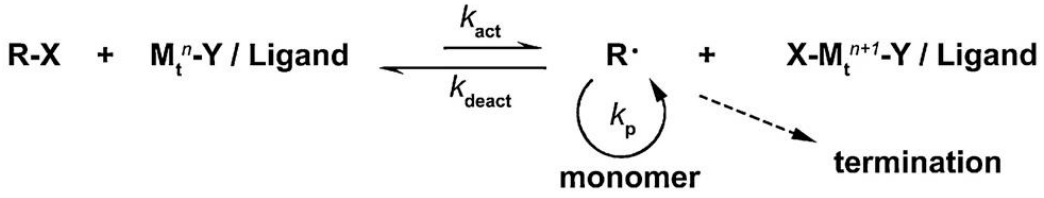


Figure 2.7 : The mechanism of transition metal-catalyzed ATRP [21, 22].

In conventional free radical polymerization, due to k_p and k_t, produced radicals propagate and terminate but in ATRP, reversible redox process catalyzed by a transition metal complex (M_t^n−Y/ Ligand, where Y may be another ligand or the counter ion) generates radicals that undergoes a one electron oxidation with consequent abstraction of a (pseudo) halogen atom, X, from a dormant species, RX.

This procedure occurs with rate constants of activation k_{act}, and deactivation k_{deact}. Polymer chains grow with the rate constant of propagation k_p, with adding radicals to monomers. By radical coupling and disproportionation termination happens and very small percentage of polymer chains go through termination in a well-controlled ATRP process, because concentration of active propagating radicals is low and dormant species' concentration is high. Despite the fact that copper is most usually used metal catalyst in ATRP, iron compounds like iron also can be used [23, 26].

The polymerization begins alkiyl halide and the transition metal in its lower oxidation state in normal ATRP. Moreover, reaction can be started with conventional radical initiator like AIBN, and the transition metal in its higher oxidation state. This reaction is named reverse ATRP [27] which radicals occurs from the (thermal) dissociation of the initiator are reversibly terminated by transition metal. Therefore, it ends up an alkyl halide and the reduced transition metal (Figure 2.8).

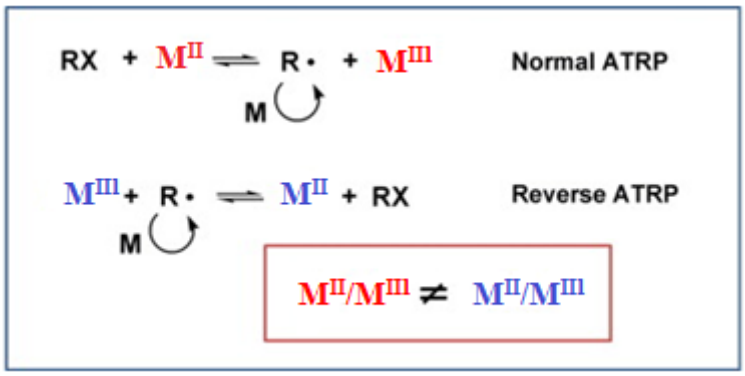


Figure 2.8 : Mechanism of normal ATRP and reverse ATRP (M: Cu, Fe, Ni etc.).

2.2.1.1 Components of ATRP

In ATRP method, usage of various components are quite important. These components are monomer, initiator with a transferable halogen and a catalyst system composed of a transition metal species and a suitable ligand. Solvent, reaction temperature, and additives are critical, too. The conditions under which a particular reaction is to be carried out must be optimized to accomplish the demanding results as a reaction occurs.

2.2.1.2 Monomers

With ATRP, one can polymerize an extensive variety of monomers such as styrenes, [28-30] acrylates, [31,32] methacrylates, [33,34] vinylpyridine, [35] and acrylonitrile

[36]. In order to have a adequately large atom transfer equilibrium the monomer must have stabilizing groups (e.g. phenyl or carbonyl) next to the carbon radical and the monomer must not have groups (e.g. acids) that meddle with the catalyst system. For preserving controll, the concentration of propagating radicals and the rate of deactivation must be arranged for each certain system. Equilibrium of the reaction relies on the radical (monomer) and the dormant species.

2.2.1.3 Initiators and halogen exchange

Alkyl halide initiates ATRP process which includes an activating substituent on the α-carbon, stabiling agent. The initiation process is carried out like propagation and the function of the initiator is to regulate how many chain will grow and generate head group of the polymer chain. When initiation is fast and transfer ande termination reactions are trivial, the number of growing chain is constant and equal to initiator concentration. The theoretical molecular weight or degree of polymerization rises reversely with initial initiator concentration and is given by equation [37]:

$$M_n = \frac{\text{grams monomer}}{\text{moles initiator}} \qquad \textbf{(2.1)}$$

2.2.1.4 Solvents

ATRP can carry out in wide range of solvents such as bulk, solution, and a heterogeneous system (for example, emulsion or suspension). A proper solvent must let minimal chain transfer to solvent and solvent promoted side reactions. In various ATRP systems, polymerization is maintained in the presence of organic non-polar media such as toluene or anisole although a wide range of solvents (e.g. diphenyl ether, ethylene carbonate, water, dimethylformamide, acetone, alcohols). Rate enhancement in polar media (e.g. using ethylene carbonate as solvent) has been observed and is attributed to a structural change in the copper complex [38]. Polar media also help to dissolve the catalyst.

2.2.1.5 Catalysts

The catalyst should be highly selective for atom transfer and should not join in other reactions in ATRP for perfect polymerization. The position of the atom transfer equilibrium and the dynamics of exchange between the dormant and active species

are determined by the catalyst. For an significant catalyst in ATRP, the metal must have at least two readily accessible oxidation states separated by one electron, have admissable affinity toward a halogen, have an expandable coordination sphere upon oxidation to suit the halogen, and be powerfully complexed to a ligand. Although a variety of metals have been used such as Fe (I) [39], Cu (II) [40-42], and Ni (II) [43-44]. This work focuses on ATRP catalyzed by copper, which is superior to other metals in versatility and costs.

2.2.1.6 Ligands

Ligands uses in ATRP to solve cataylsts in the media. Ligands such as N, N, N, N, N''-pentamethyldiethylene triamine (PMDETA) 1,1,4,7,10,10 hexamethyltriethylenetetramine (HMTETA), and tris[2 (dimethylamino)ethyl]amine (Me_6TREN) [45] are used in ATRP system. Ligand behavior is effected by electronic and steric effects of the ligand [46, 47]. Choosing appropriate ligand for the ATRP system is quite vital. Catalytic systems have been used in both heterogeneous and homogeneous media. Early ATRP researches comparing bipy ligands with and without solubilizing alkyl groups proved that the soluble catalyst systems resulted in lower polydispersities, similar initiator efficiencies, and slower overall polymerization rates as compared to the heterogeneous bipy systems [48]. The increased control is grounded on better solubility of the copper (I) species which causes deactivation.

Homogeneous systems has the superiority of contributing detailed kinetic and mechanistic studies of the polymerization [49,50] haupt and coworkers [51] have studied ATRP of styrene with various bipy and diimine ligands with CuBr catalyst and indicated that ligand structures and steric restraints have an important impact on catalyst activity, which demonstrates itself either as incomplete initiation, slow deactivation, or a combination of both.

2.3 Properties and Characterization of Functionalized Polymers

Functional polymer chemistry and technology has made impressive progress in recent years since the first generation of ion-exchange resins and membranes. For instance, preparation and design of several enzyme and nucleic acid models have

moved on considerably and the improvement of the technology necessary to use these polymers is living interest.

There are numerous assessments in the choice of the functional polymers to be used in a particular application functionalized polymers must have a structure which allows sufficient of reagent in the reactive sites. This relies on the width of the efficient pore size, pore volume (porosity) and the chemical reaction on reaction sequence. This in turn depends on the degree of the crosslinking of the resin and the conditions employed during its preparation [52].

Functional polymers is used to remove reactive dyes, borons, mercury and their derrivatives from wastewater.

2.3.1 Grafting Techniques

Today, there is great interest to the polymers having nonlinear architecture with different composition and topology such as star, miktoarm star, graft, hyperbranched, dendrimer, and cyclic structures [53,54].

An important category of three-dimensional macromolecular architectures with many examples detailing their single molecule visualization is consisted by brush and block graft copolymers and thanks to their unique properties, these graft polymers take great attention [55,56]. Block graft copolymers might be classified through one of three general synthetic methods: “grafting from”, “grafting through,” and “grafting onto” (Figure 2.9).

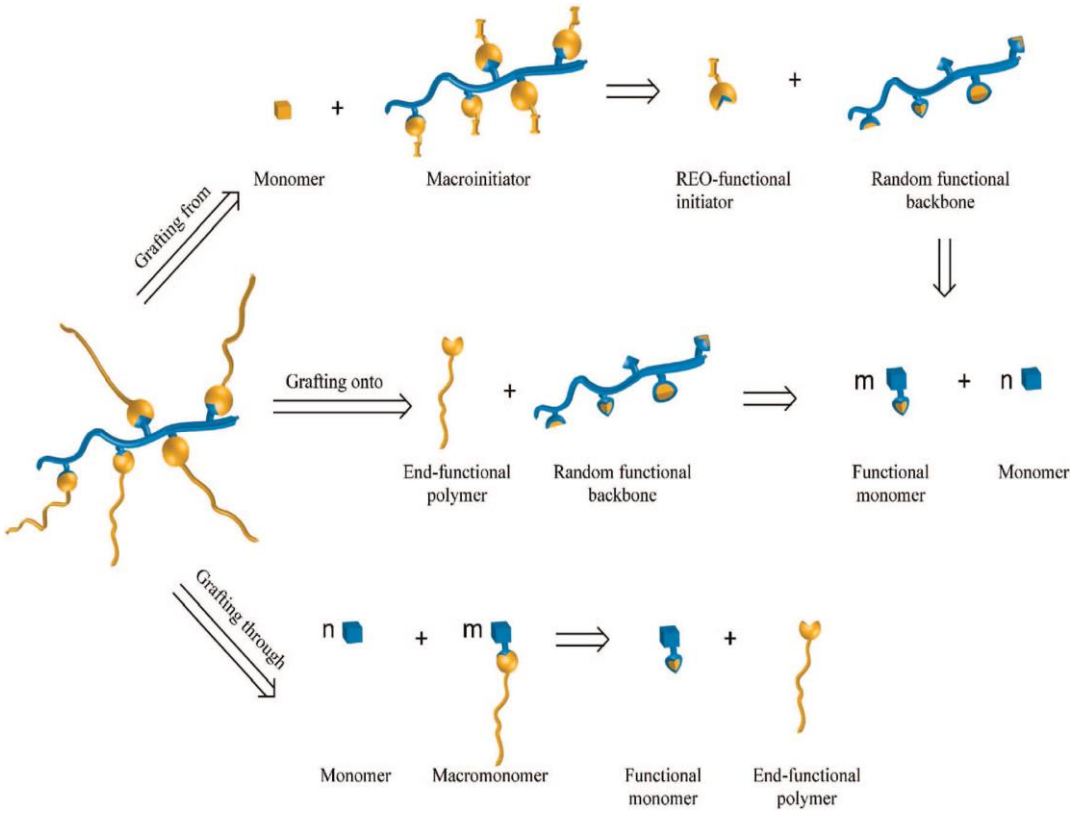


Figure 2.9 : "grafting from" (upper), "grafting onto" (middle), "grafting through" (lower) techniques [57].

2.3.1.1 Grafting from strategy

In "grafting from" strategy, there is a backbone which has active sites and they initiate the polymerization (Figure 2.9, upper). Therefore, graft copolymer can occur due to these initiating sites. This approach has been used widely to obtain brush or comb-like copolymers. A number of graft copolymers can be synthesized using only a single grafting from method [9,58].

2.3.1.2 Grafting through strategy

The "grafting from" method comprises preformed macromonomers that will be polymerized to produce graft polymer (Figure 2.9, lower portion). Due to the macromonomers which are polymeric or oligomeric chains with a polymerizable end group, the backbone is formed *in situ*. This method has been utilized to synthesize graft copolymers using a variety of controlled polymerization techniques. Owing to requirement of specific polymerizable chain end functionality and the steric effects that can effective polymerization of high molecular weight or bulky macromonomers the grafting through technique is complicated.

2.3.1.3 Grafting onto strategy

The grafting density of polymeric brushes made using the "grafting onto" technique is typically low due to the steric closeness that happens when trying to couple polymer chains onto a backbone (Figure 2.9, middle). One strategy used to increase the grafting density is the employment of highly efficient organic chemistries that will enhance the range of reaction between the polymeric grafts and the backbone.

2.3.2 Crosslinked Polymers and Their Properties

"Physiosorption", "grafting" and "crosslinking" are the methods by which the merger of monomers and polymers is described. Physiosorption depends on physical attractive forces which is reversible. This technique, can be accomplished by using functionalized polymers on to the solid surface or self - assembly of polymeric surfactants. Grafting technique is irreversible and covalent bonds occurs in this process. Crosslinking has same properties as grafting. The schematic presentation of all the processes is depicted in (Figure 2.10 A). It may be intra - and intermolecular (Figure 2.10 B).

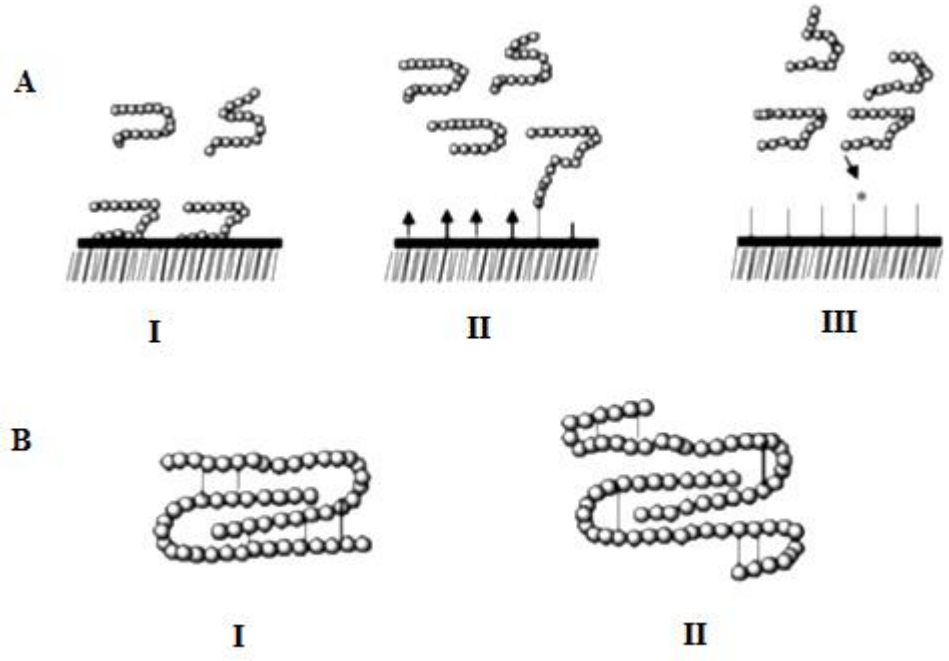


Figure 2.10 : (I) physiosorption, (II) grafting onto, (III) grafting from. B (I)intermolecular (II) intramolecular crosslinking.

In this thesis, crosslinked polymers are studied. By using these polymers some advantages can be obtained, such as:

- They suggest greatest is of processing because of their solubility.
- They can be arranged in spherical bead structure and can be discriminated from low molecular weight contamined by using simple filtration technique and can be washed with very use solvents.
- Low crosslinked resins swell massively, revealing their inner reactive groups to the soluble reagents.
- Polymer beads with very low degrees of crosslinking can be prepared with very porose structures which allow solvents and reagents to diffuse inside of the beads to contact reactive groups.

Compared to conventional polymers, grafted and/or crosslinked polymers are prepared by the modification of polymers are attractive because of their new or improved properties. These new or improved features grow mainly from the introduction of new functionalities and/or interlinkages to the original polymers structures by grafting and/or crosslinking reactions. Usage of grafted and/or crosslinked polymers has found a consistant place in various areas such as separation processes, energy conversion, solid state, biomedical, biological, and environmental applications because their chemical and physical properties can be tailored over a wide range of characteristics.

2.3.3 Classification of grafted and/or crosslinked polymers

As shown in Figure 2.11 grafted and/or crosslinked polymers are present in different forms that change in their classifications. These polymers can have different physical forms like gels, resins, fibers, films, and fabrics that have widely differing chemical and physical properties and can be chemically active. Greater number of these polymers are modified syntheticpolymers such as polyethylene, polystyrene, and polyvinyl fluoride on the other hand, some of them modifed natural polymers including chitosan, starch, and cellulose. grafted and/or crosslinked polymers can be classified into various categories including ion exchangers, chelating adsorbents, hydrogels, and affinity polymers in view of the seperation function (Figure 2.12).

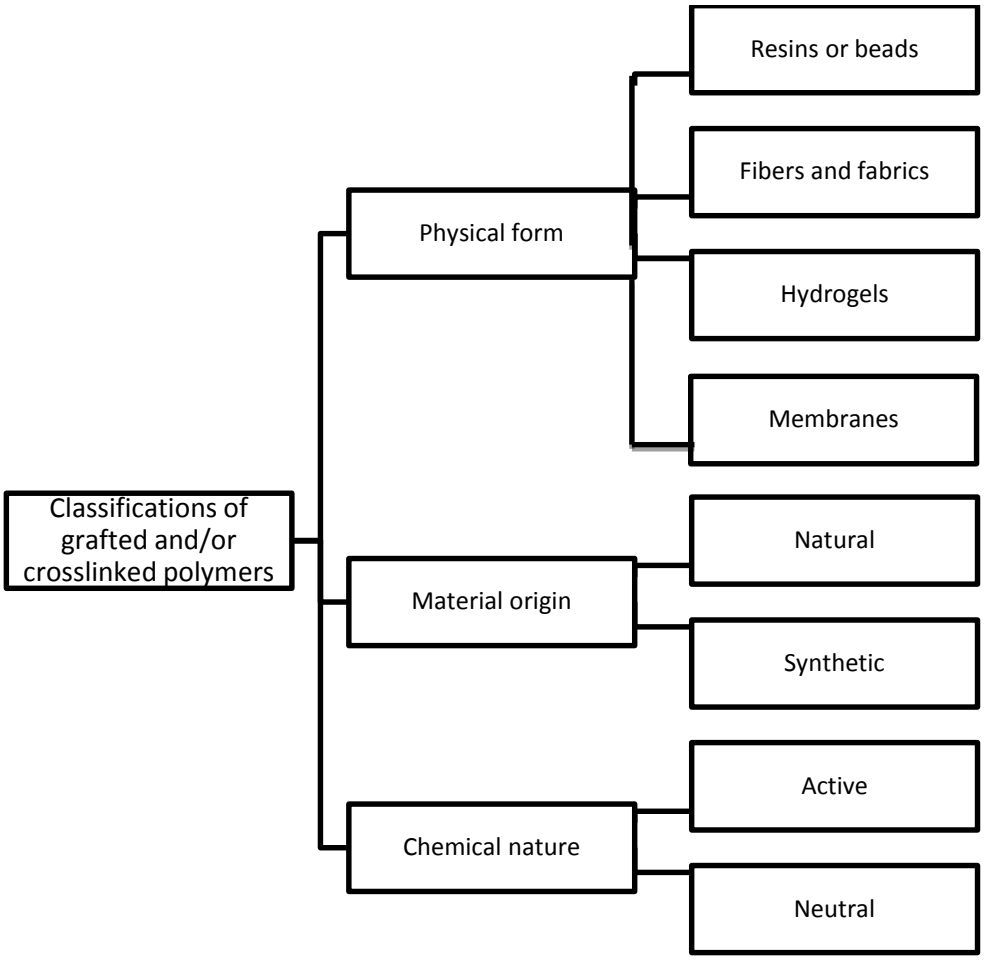


Figure 2.11 : A schematic representation for various classifications of grafted and/or crosslinked polymers.

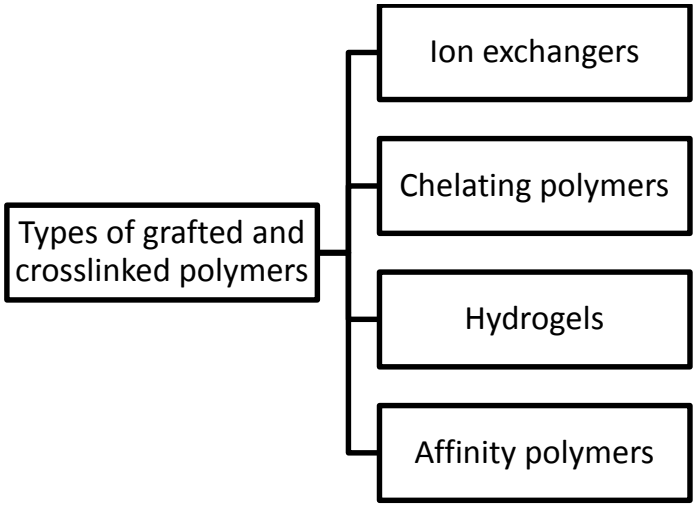


Figure 2.12 : A schematic representation for various types of grafted and/or crosslinked polymers.

Ion exchange resins have found widespread applications in various fields including water and waste water treatment; oil and gas, electronics, electroplating, and tanning

industries; sugar decolourizations; starch hydrolysated deionization; acid catalysis of sucrose; steam flooding; and the improvement of soil water retention.

2.4 Hazardous of Dyes

The most critical and fundamental component in the world for vital activities of living beings is water. Because of geometrical growth of population, industrialization, civilization, domestic, and agricultural activities, and other geological and environmental changes water quality of our water resources is getting worse. Hence, water pollution has become an important issue now, effecting all living creatures, household, recreation, fishing, transportation, and other commercial activities and government authorities, scientists, and academicians are concerning about it. Some water contaminants such as organic, inorganic, and biological pollutants have serious side effects and toxicities with a few being lethal and carcinogenic. Aquatic conditions, and the ecosystem of the earth as a whole are threatened by these pollutants.

Dyes which are used by many textile manufacturers release aromatic amines (e.g., benzidine, toluidine). Dyebath effluents may contain heavy metals, ammonia, alkalai salts, toxic solids and large amounts of pigments - many of which are toxic. Natural dyes are rarely low-impact, depending on the specific dye and mordant used which a substance used to "fix" the color onto the fabric such as chromium are very toxic and high impact. The wide quantities of natural dyestuffs demanded for dyeing, typically equal to or double that of the fiber's own weight, make natural dyes prepared from wild plants and lichens very high affect.

Because of their ease of use, inexpensive cost of synthesis, stability and variety of colour compared with natural dyes, synthetic dyes have been progressively used in the textile, paper, rubber, plastic, cosmetics, and pharmaceutical and food industries. Present, there are more than 10,000 commercial dyes available. Due to their complex aromatic molecular structure and synthetic origin, most of synthetic dyes are not biodegradeble. The broad use of dyes generally poses pollution problems in the form of coloured wastewater discharge into environmental water bodies, which interferes with transmission of sunlight into streams thus reduces photosynthetic activity. Besides, some dyes or their metabolites are either toxic or mutagenic and carcinogenic. The presence of these heat and light stable, complex dye molecules in

wastewater made the conventional methods of sewage treatment, such as primary and secondary treatment systems, unsuitable. The adsorption process provides an attractive alternative treatment, especially if the adsorbent is inexpensive and readily available.

Acid dyes are sodium salts of organic sulfonic acids. Brightly colored, water soluble and reactive acid dyes are composed of ionizable anionic groups such as sulfonates, carboxylates or sulfates (Figure 2.13).

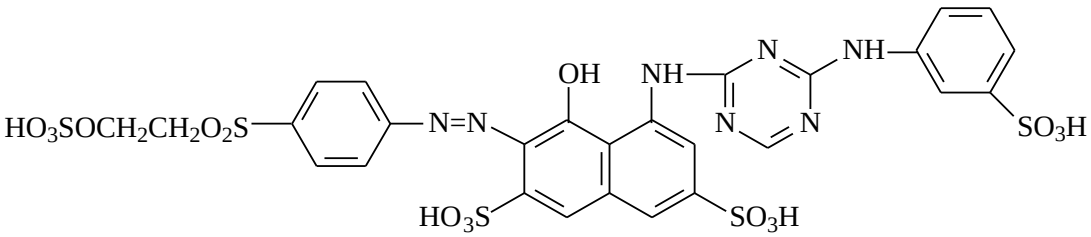


Figure 2.13 : Chemical Structure of Reactive red.

2.5 Technologies Available for Color Removal

Techniques of dye wastewater treatment have been reviewed by Pokhrel and Viraraghavan [59], Slokar and Majcen Le Marechal [60], Dele´e et al. [61] and Cooper [62]. Fungal and bacterial decolorization methods have been reviewed by Aksu [63], Wesenberg et al. [64], Fu and Viraraghavan [65] and Stolz [66].

There are several reported methods for the removal of pollutants from effluents (Table 2.2).

Table 2.3: Principal existing and emerging processes for dye removal.

	Technology	Advantages	Disadvantages
Conventional Treatment Proceses	Coagulation Flocculation Biodegradation	Simple, Economically feasible Economically,attractive,publicly acceptable treatment	High sludge production, handling and disposal problems Slow process, necessary to create an optimal favorable environment, maintance and nutrition requirements
	Adsorption on activated carbons	The most effective adsorbent, great capacity, produce a high-quality treated effluent	Ineffective against disperse and vat dyes, the regeneration is expensive and results in loss of the adsorbent, non-destructive process
Established recovery process	Membrane seperations	Removes all the dye types, produce a high-quality treated effluent	High pressures, expensive, incapable of treating large volumes
	Ion-exchange	No loss of sorbent on regeneration, effective	Economic constraints, not effective for disperse dyes
	Oxidation	Rapid and efficient process	High energy cost, chemical required
Emerging removal process	Advanced oxidation process	No sludge production, little or no consumption of chemicals, efficiency for recalcitrant dyes	Economically unfeasible, formation of by-products, technical constraints
	Selective bioadsorbents	Economically attractive, regeneration is not necessary, high selectivity	Requires chemical modification, non-destructive process
	Biomass	Low operating cost, good efficiency and selectivity, no toxic effect on microorganisms	Slow process, performance depends on some external factors (pH,salts)

This technologies can be classified into three categories which are biological, chemical and physical.

Today, there is not single process capable of sufficient treatment, essentially because of the complex nature of the effluents [35,36]. In practice, a combination of different processes is often used to gain the required water quality in the most economical way.

2.5.1 Biological treatments

Compared with other physical and chemical processes, biological treatment is generally the most inexpensive option. Due to many microorganisms such as

bacteria, yeasts, algae and fungi has ability to accumulate and degrade various pollutants, biodegradation methods such as fungal decolorization, microbial degradation, adsorption by (living or dead) microbial biomass and bioremediation systems are implemented to the treatment of industrial effluents. However, because of technical shortages, their implementation is restricted. These shortages are requirement of large land area, sensitivity toward diurnal variation as well as toxicity of some chemicals, and less flexibility in design and operation [37]. Sufficient color elimination can not be done with current conventional biodegradation processes. Additionally, in spite of many organic molecules are degraded, owing to their complex chemical structure and synthetic organic origin, many others are obstinate [30]. Particularly, azo dyes are not totally degraded because of their xenobiotic nature.

2.5.2 Chemical methods

Chemical methods such as coagulation, flocculation, irradiation or electrochemical processes are useful for dye removal but very expensive and they bring about disposal problems because of accumulation of concentrated sludge. Moreover due to excessive chemical usage, there will be secondary pollution problem. Nowadays, advanced oxidation process based on the generation of very powerful oxidizing agents such as hydroxyl radicals, have been implemented efficiently for pollutant degradation. However, chemical methods requires high electrical energy and chemical reagents are consumed highly. These are common shortages in chemical treatment.

2.5.3 Physical methods

Various physical methods like membrane-filtration (nanofiltration, reverse osmosis, electrodialysis, etc.) and adsorption techniques are extensively used. However membrane processes have some shortages such as having limiting lifetime before membrane fouling occurs. Moreover, the the expense of regular replacement affects economic viability badly. On the other hand, liquid-phase adsorption is one of the most favoured technique for removal of pollutants from wastewater due to its produced effluent has high-quality. Concerning the sorbent is inexpensive and does not need an additional pre-treatment step before its application, adsorption process is

seen an efficient alternative for water treatment. Overall, adsorption is a great separation process and significant technique for pollutant removal [67].

2.6 Adsorption

Gaseous or liquid components are kept by porous solids with their external and/or internal surface in adsorption process. Adsorption can be divided into three categories owing to their bonding types:

(a) Physical adsorption: Physical adsorption consists intermolecular interactions between energy sites and does not have chemical bonding. Surface holds adsorbate with weak Van der Waals forces and multiple layers can be occured.
(b) Chemical adsorption: In chemical adsorption, electron exchanges occurs between specific surface sites and solute molecules so chemical bond is formed. Usually, only a single molecular layer can be adsorbed.
(c) Electrostatic adsorption (ion exchange): This process is generally categorized as ion-exchange and Coulomb forces between ions and charged functional groups is penetrative.

The surface of the adsorbent is not smooth which exhibit valleys and peaks at a microscopic level. These areas are sensitive to force fields in which the atoms of the solid appeal to atom sor molecules from a fluid nearby. The pore structure of the sorbent is the most significant feature for adsorption. Adsorption capacity is determined by total number of pores, their shape and size.

2.6.1 Environmental Applications of Adsorption

A number of environmental applications of adsorption are present and many others are being devoloped (Noble and Terry, 2004).

Adsorption can be used in (Noble and Terry, 2004; Dabrowski, 2001):

- Water treatment in organic solvents
- Organics treatment in water
- Setting taste and odor for wastewater treatment
- Elimination of radon, hydrogen sulfide, and other sulfur compounds from gas streams

- Removal of heavy-metal in clay barriers
- Solvent healing and solvent vapor fractionation
- Elimination of water from gas streams containing acid gases

“Greenhouse” gases such as carbon monoxide, methane are used for adsorption, the employment of methane, the flue gas treatment (SO_x, N_x, Hg removal).

Adsorption process has both superiorites and shortcomings [68].

Superiorities:

- Significant removal
- Ability of removal refractory and/or toxic organic compounds
- Easy installation and maintenance
- Wide variety of adsorbents accesible

Shortcomings

- Adsorbents decline in capacity gradually
- Particulates in the process is a problem
- high content of macromolecular compounds reduces efficiency and can cause irreversible blockage of active sites
- requirement of regenaration for spent adsorbent
- high capital cost

2.6.2 Characteristics of Sorbent Materials

Commercial sorbents used in adsorption processes should have the following qualifications:

- Wide selectivity derived from equilibrium, kinetic, or steric effect;
- Wide adsorption capacity;
- Quick adsorption kinetics;
- Simply regenerable;
- Well mechanical strength;
- Low cost.

The adsorbent performance requirements can easily transfer to adsorbent characteristic requirements as follows:

- Wide internal pore volume;
- Wide internal surface area;
- Controlled surface features through selected functional groups;
- Managing pore size distribution, preferably in micropore range;
- Weak interactions between adsorbate and adsorbent (mostly on physical sorbents);
- Inorganic or ceramic materials to enhance chemical and mechanical stability.

2.6.3 Color Removal Using Commercial Activated Carbons

Due to remove chemical pollutants from wastewater, solid sorbents are extensively used employing adsorption method. In spite of wide range of solid materials are purposed, activated carbon is one of the most common material for pollutant removal from waste water [38,69]. Considering other expensive materials, activated carbon (CAC) is a favorrable alternative to them because of its great capacity to adsorb dyes. CAC have porous structure which let them a large surface area, and in order to upgrade their properties, they can be modified by chemical treatment. On the other hand, CAC have shortcomings such as expensiveness, non-selectiveness and ineffectiveness against disperse and vat dyes. Adsorbent can be lost while regeneration of saturated carbon and this process is quite expensive. Utilizing carbons depends on relatively high-priced starting materials is also unjustified for most pollution control applications [39]. This situation has caused many researches to work for more economic adsorbents.

2.6.4 Clays

Since the early days of civilization, natural clay minerals are commonly known by humans. Clays are powerful alternatives for adsorbents due to their cheapness, accesibility of all over the world, great sorption capacities and potentiality for ion-exchange. Clay materials have layers in their structure so their sorption capacities arise because of their high surface area and high porosity [46]. Due to negative charges on the structure of minerals, clays can adsorp positively charged species.

Nowadays, there has been a considerable arise in the usage of clay minerals such as bentonite, kaolinite, diatomite because of their capability to adsorp both inorganic and organic molecules. Especially, interactions between dyes and clays has been widely studied [70-81] due to clays intense affinity both heteroatomic cationic and anionic dyes. The process of adsorption between dyes and clays based on ion-exchange procedure which means sorption capacity can vary with pH values.

2.6.5 Siliceous materials

Due to their presence on earth, accessibility and low-cost, natural siliceous materials such as silica beads, glasses, alunite, perlite and dolomite are utilized progressively for wastewater treatment. Owing to their chemical reactivity of their hydrophilic surface, resulting from the presence of silanol groups, silica beads takes particular interest [47,82-84]. They involve porous areas, high surface and mechanical stability so these features make them suitable for adsorbing but because of their low endurance toward alkaline solutions they can not be used less than pH 8 [85]. Also, they involves acidic silanol groups that creates powerful and generally irreversible non-specific adsorption. Therefore, getting rid of negative properties of the sorbent is quite important.

Alunite which contains about 50% silicium dioxide (SiO_2) is one of the siliceous materials to adsorb dye molecules [86-88]. However it has not proper adsorbent features. Alunite-type layered compounds can be used in color removing after a suitable process.

Also, dolomite, perlite and glass have been suggested for dye uptake. Dolomite which is both mineral and rock, removal capability for dye removal has been estabilished [89]. Perlite which is a glassy material, has a high silica content and it is cheap, easily available in many regions. Perlite is a good adsorbent but its several types (expanded and unexpanded) and of different origins have different features owing to the differences in composition.

2.6.6 Zeolites

Zeolites which has various cavity formations are highly porous aluminosilicates. They are negatively charged and this charge is equalized by cations which can be exchangable with certain cations in solutions. Zeolites are appealing sorbents

because of their high ion-exchange capacity relatively high specific areas and low-cost. Owing to zeolites rigid porous structures, they have ion selectivity. They have been researched profoundly due to their capability in removing trace quantities of pollutants such as heavy metal ions and phenols thanks to their cage-like structures suitable for ion exchange. They are also proper sorbent for removal of dyes. Natural zeolites are studied severally on the sorbent behavior [48-50]. However, raw clinoptilolite which is a type of zeolites does not suitable for the removal of reactive dyes due to extremely low sorption capacities [51]. Nearly the same results have been found by Ozdemir et al. and Benkli et al. [90]. They proposed chemical modification with quaternary amines as a means of increasing sorption. The real applicability of these natural materials to purify dye waste waters is still quite unknown in spite of the promising results. Zeolites requires an artificial support when used in column operations which causes another problem.

2.6.7 Biosorbents

Biosorption which means accumulation and concentration of pollutants from aqueous solutions by the use of biological materials, is used for color removal too. In order to concentrate and remove dyes in wastewater, biological substances like chitin, chitosan, peat, yeasts, fungi or bacterial biomass are utilizing as chelating and complexing sorbents by their functional groups which can complex with dyes. Biosorption technique is unique, penetrating and low-cost way for removal of pollutants. Moreover, it is more selective than traditional ion-exchange sorbents and commercial activated carbons. Dye concentrations in contaminated water can be reduced to ppb levels by using biosorbents.

2.6.8 Chitin and chitosan

Chitin and chitosan which are abundant, regenerable and biodegradable, are estabilished as emerging biosorption methods for dye removal even at low concentrations. Chitin can be found in various natural sources like crustaceans, fungi, insects, annelids and mollusks but it can only extracted from crustaceans (crab, krill, crayfish) because of crustacean’s exoskeleton is available as a by-product of food processing. Also, it can be helpful for economy to use industrial solid wastes for the treatment of wastewater from another industry.

Wong et al. investigated chitosan as an adsorbent to remove acid dyes and found its capacity for acid orange 12, acid orange 10, acid red 73 and acid red 18 were 973.3, 922.9, 728.2, and 693.2 mg/g, respectively.

For absorption of anionic dyes, chitosan-based biosorbents have superb performance compared with activated carbon. Therefore chitosan chelation is proper method for dye removal from wastewater but chitosan has low affinity for cationic (basic) dyes.

Utilizing chitosan brings about shortcomings too. The adsorption features can alternate with different sources of chitin, the degree of N-acetylation, molecular weight and solution properties, crystallinity, affinity for water, percent deacetylation and amino group content. These factors effect biopolymers characteristics, materials type affects performance and accessibility of sorption regions influence efficiency of adsorption. Adsorption is considerably depending on pH. Dye molecules has different and complicated structures which is important parameters influencing adsorption. There is, as yet, little information in the literature on this issue. The conventional and trading resource of chitin is from shells of crab, shrimp and krill that are wastes from the processing of marine food products. However, this traditional method of extraction of chitin makes its own environmental problems as it generates large quantities of waste and the production of chitosan also consists a chemical deacetylation process. These problems can why it is difficult to develop chitosan-based materials as adsorbents at an industrial scale.

2.6.9 Peat

Peat which has a porous structure, is a complex soil material with organic matter in different levels of decomposition. This natural sorbent which is abundant, cheap and easily accessible, generates adsoprtion of different pollutants due to its polar character [91-93]. According to Allen et al. this sorbent has cation exchange ability, and can rmove dyes effectively. The removal capacity can be compared with activated carbon for acid and base, also the performance is much better in disperse dyes.

Due to natural peat has properties such as low mechanical strength, a high affinity for water, poor chemical stability, a tendency to shrink and/or swell, and to leach fulvic acid, raw peat can not be used directly [94,95] so it should be chemically modified to heal sorption properties and selectivity.

Adsorption mechanism of dyes onto peat is unknown. Various studies has different results. Mechanisms such as physical adsorption, ion-exchange, complexation, adsorption–complexation and chemisorption are thought to be in the biosorption process [96]. Wide range of peat types and preparation of sorbent generate the comparison of results difficult but it is now thought that ion-exchange is the most prevalent mechanism.

2.6.10 Biomass

Recently many studies have concerned about biomass such as fungi and other microbial cultures for bioadsorption. Due to some dyes have affinity to microbial species, biomass can be used for wastewater treatment [97,98]. Biomass is a biosorbent which is abundant and has low price so usage of it is increasing. While sythesizing valuable products like antibiotics and enzymes, a large amount of by-product occurs and they can be used in biosorption of pollutants. A wide range of microorganisms such as algae, yeasts, bacteria and fungi has ability to decolorize various dyes with a high efficiency due to their physico-chemical characteristics [99-101].

Biosorbent material has low-cost and effective in reducing the concentration of dyes to very low levels. For instance, fungal biomass can be generated inexpensively by using easy fermantation methods and cheap growth media [102]. Biomass can be used even the dye is very toxic. Moreover, biosorption is an emerging technique which attempts to cope with selectivity disadvantage of conventional adsorption processes. The use of that rather than live biomass takes away the issues of waste toxicity and nutrient requirements. Biomass adsorption is significant when conditions are not always favorable for the growth and maintenance of the microbial population.

2.6.11 Polymeric Adsorbents

Various synthetic, nonionic polymers are used as sorbents, ion-exchange resins and particularly for analytical chromatography applications. These polymers are available in markets copolymer forms of styrene=divinyl benzene and acrylic acid esters=divinyl benzene which are in bead form (typically 0.5mm in diameter) and they have different surface polarities, porosities and macropore sizes. Utilizing suspension polymerization, porosities can be obtained in the media of a solvent that dissolves the monomers and serves as a poor swelling agent for the polymer.

Polymer matrix with surface areas can be made by porosity [103,104]. Water treatment is one of the common application for polymeric adsorbents. To imitate activated carbon, functional groups can be attributed on polymeric sorbents and it can be used for certain specific applications in food and pharmaceutical industries where activated carbon is used to be. Polymeric adsorbents can be regenerated effortlessly and they results significantly in dye removal.

3. EXPERIMENTAL

3.1 Materials and Method

2-(Dimethylamino) Ethyl Methacrylate (Aldrich), Vinyl Benzyl Chloride (Fluka), Ethylene Glycol Dimethacrylate (EGDMA) (Fluka), PMDETA (Aldrich), CuBr (Aldrich), $CuBr_2$ (Aldrich), Polyvinyl Alcohol (PVA) (Fluka), Calcon (E-Merck), Everzol Black (Aldrich), Reactive Red (Aldrich) and all chemicals used were analytical grade commercial products.

UV-Vis Spectrophotometer (Perkin-Elmer Lamda 25), FT-IR Spectrophotometer (Nicholet) and orbital shaker were used.

3.2 Preparation of Polymeric Sorbents

Two different polymeric sorbents were synthesized for dye removal.

3.2.1 Preparation of Crosslinked 2-(dimethylamino) Ethyl Methacrylate (DMAEM) Beads

Crosslinked 2-(dimethylamino) ethyl methacrylate beads were prepared by suspension polymerization. 2-(dimethylamino) ethyl methacrylate (15.0 mL, 0.09 mmol), EGDMA (1.9 mL, 0.01 mmol), and AIBN (0.5 g, 3.04 mmol) were dissolved in toluene (10 mL). The resulting solution was dispersed in an aqueous medium, prepared by dissolution of PVA (1.0 g) in water (200 mL). The polymerization was carried out in a magnetically stirred glass flask (250 mL) at 70 °C for 24 h. After polymerization, polymeric beads were washed exhaustively with excess of water and acetone to remove the diluents and unreacted monomer. They were subsequently dried in vacuo at room temperature. The beads were sieved and a proper size fraction (200-500 μm diameters) was isolated. The yield was 9.83 g.

3.2.1.1 Determination of the amine content of crosslinked DMAEM beads

0.1 g of beads and 10 mL of 0.1 M hydrochloric acid solution (HCl) were added to the 50 mL of erlen. This mixture was stirred for 24 h at room temperature. Then, the

solution was filtered to remove beads and unreacted HCl solution was titrated with 0.05 M sodium hydroxide solution (NaOH). Amine content of the beads was found as 1.075 mmol.g^{-1} resin.

3.2.2 Preparation of Polyvinyl Benzyl Chloride (PVBC) Beads

Crosslinked PVBC microspheres were prepared by suspension polymerization according to the literature. The details are as follows:

VBC (5.0 mL, 31.9 mmol), EGDMA (1.5 mL, 7.8 mmol), and AIBN (0.12 g, 0.71 mmol) were dissolved in toluene (7.2 mL). The resulting solution was dispersed in an aqueous medium, prepared by dissolution of PVA (0.25 g) in water (80 mL). The polymerization was carried out in a magnetically stirred glass flask (100 mL) at 78 °C for 8 h. After polymerization, the PVBC microspheres were washed exhaustively with ethanol, and then with water, to remove the diluents and unreacted monomer. They were subsequently dried in vacuo at 50 °C. The microspheres were sieved and a proper size fraction (200-500 μm diameters) was isolated.

3.2.3 Grafting of 2-(dimethylamino) ethyl methacrylate beads onto (PVBC) Beads

$CuBr_2$ (0.0075 g, 0.03 mmol), PMDETA (0.14 mL, 0.675 mmol) were dispersed after ultrasonication in toluene (9.8 mL) for 5 min. 2 g of PVBC were added and the mixture was deoxygenated via nitrogen gase. Then CuBr (0.486 g, 3 mmol) and 2-(dimethylamino) ethyl methacrylate (10 mL, 54 mmol) was introduced into the flask under nitrogen flow. At the end, the mixture was degassed and immersed in an oil bath to preheat at 60°C for 24 h to polymerize. After reaction, the mixture was filtered and was interact with EDTA solution to remove copper catalyst. The product was dried under vacuum at room temperature for 24 h and the yield was 5.06 g.

3.2.3.1 Determination of the amine content of 2-(dimethylamino) ethyl methacrylate graft PVBC Beads

To 6 mL of 0.1 M HCl 0.06 g of the amine containing sorbent was added and left to stand overnight. The mixture was filtered and titrated with 0.05 M (NaOH) the resulting 6 mL of the titrant indicates 5.42 mmol.g^{-1} amine content.

Moreover, the core-shell was characterized by using FT-IR spectroscopy.

3.2.4 Dye Uptake Measurements of the sorbents

Dye capacities of the both sorbents were determined by mixing a weighed amount of polymer sample (0.1 g) with 20 mL aqueous dye solution (2 g dye/100 mL water). In these experiments, the dyes Calcon, Everzol Black and Reactive Red were used. The mixture was stirred for 24 h and then filtered. The dye concentrations were determined colorimetrically at different wavelengths and the dye loading capacities were calculated from the initial and final dye contents of the solution. 1ml of the filtrate was used for determination of the residual dye.

Also dye sorption capacities were found at different pH values different concentrations and different ion concentrations.

3.2.4.1 Kinetics of the Dye Sorption

To estimate the efficiency of the sorbents for trace dye removal, batch kinetic experiments were performed using highly diluted dye solutions (10^{-4} g dye /L water). For this purpose, sorbent (0.1 g) was wetted with distilled water (1 mL) and added to a solution of dye (100 mL). The mixtures were stirred magnetically and aliquots of the solution (5 mL) were taken at appropriate time intervals for analysis of the residual dye. Moreover, kinetic of grafting with ATRP is studied.

3.2.4.2 Regeneration of the Sorbent

The dye loaded samples (0.1 g) were interacted with 10 mL of potassium hydroxide (KOH) (0.9 mol L^{-1}) and stirred at room temperature for 24 h. Then mixture was put into oil bath at 75°C for 2 h. After cooling, the mixtures were filtered, and 2 mL of the filtrate was removed for colorimetric analysis of the dyes. Regeneration capacity of the core-shell was found as 0.83 g dye / g resin (92.8 %) for Reactive Red.

4. RESULTS AND DISCUSSION

In this study, two polymeric sorbents were prepared. Crosslinked poly 2-(dimethylamino) ethyl methacrylate-co-EGDMA resin was prepared by using suspension polymerization method.

Other core-shell type polymeric sorbent was prepared starting from crosslinked PVBC resin. The poly (2-(dimethylamino) ethyl methacrylate) was grafted onto PVBC resin by using inverse ATRP technique.

4.1 Preparation of Crosslinked 2-(Dimethylamino) Ethyl Methacrylate Beads

Crosslinked poly (2-(dimethylamino) ethyl methacrylate) was synthesized with crosslinking reaction between 2-(dimethylamino) ethyl methacrylate monomer and EGDMA (10% mole) as a crosslinker by using suspension polymerization method at 70 ^{0}C for 24 h (Figure 4.1).

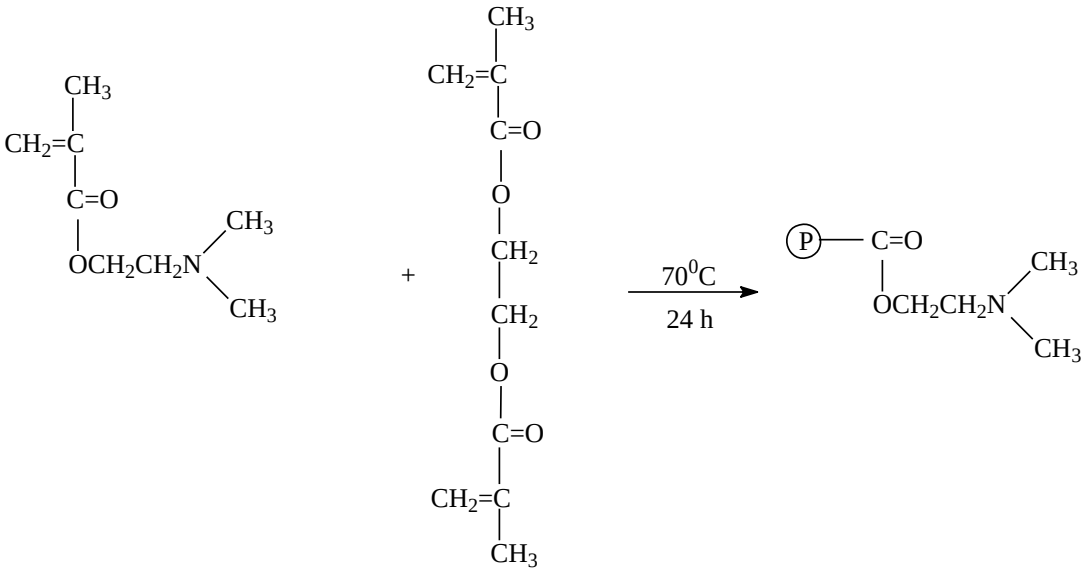


Figure 4.1 : Crosslinking 2-(dimethylamino) ethyl methacrylate with EGDMA.

4.2 Preparation of Polyvinyl Benzyl Chloride (PVBC) Beads

This resin was synthesized starting from crosslinked polyvinyl benzyl chloride-EGDMA (10%) in the presence of AIBN as initiator, poly (vinyl alcohol) as stabilizator and as toluene as porogen at 78 ^{0}C for 8 h (Figure 4.2).

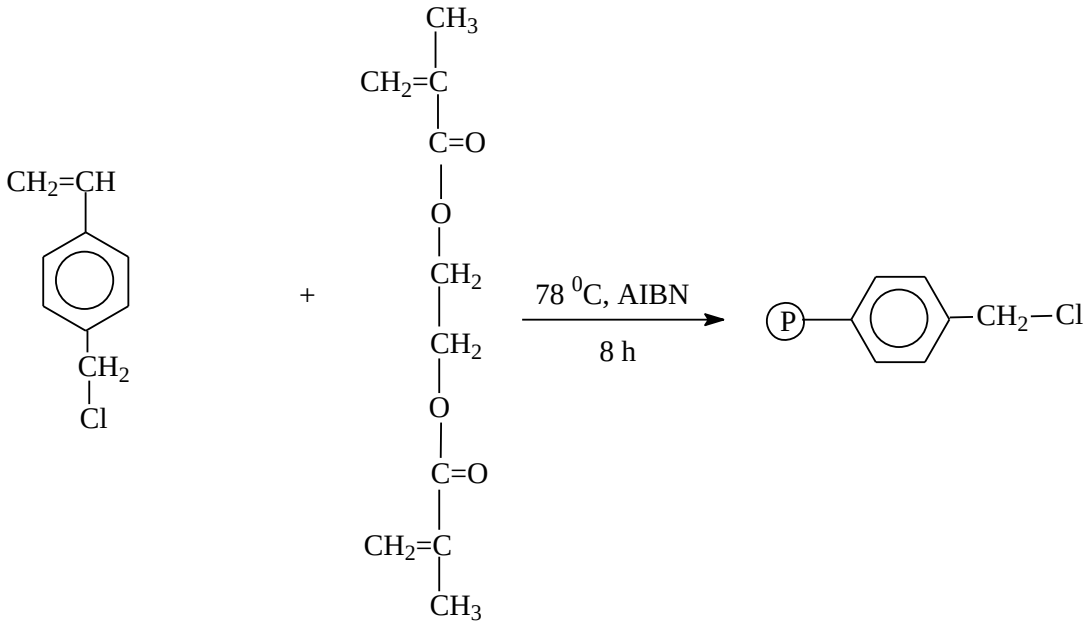


Figure 4.2 : Preparation of Polyvinyl Benzyl Chloride (PVBC) Beads.

4.3 Grafting of 2-(dimethylamino) Ethyl Methacrylate Beads onto (PVBC) Beads

2-(dimethylamino) ethyl methacrylate was grafted onto PVBC beads by ATRP method (Figure 4.3). The most important feature of the AIBN initiated polymerization technique for grafting vinyl monomers is that it proceeds via single electron transfer with the formation of free radicals on reducing agent. This method of grafting yields substantially pure graft copolymer since the free radicals are produced exclusively on the backbone. Core-shell structure is occurred by using this method (Figure 4.4).

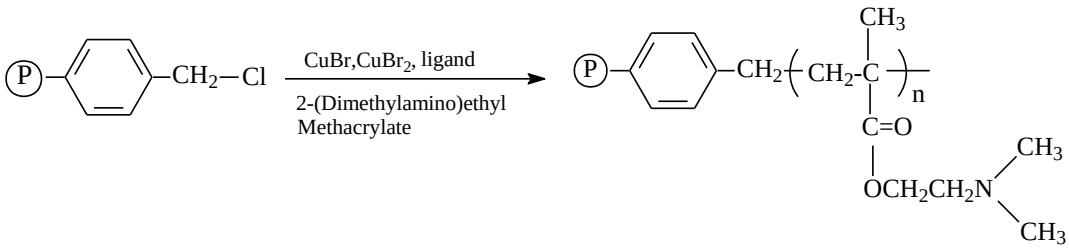


Figure 4.3 : Grafting of 2-(dimethylamino) ethyl methacrylate onto PVBC.

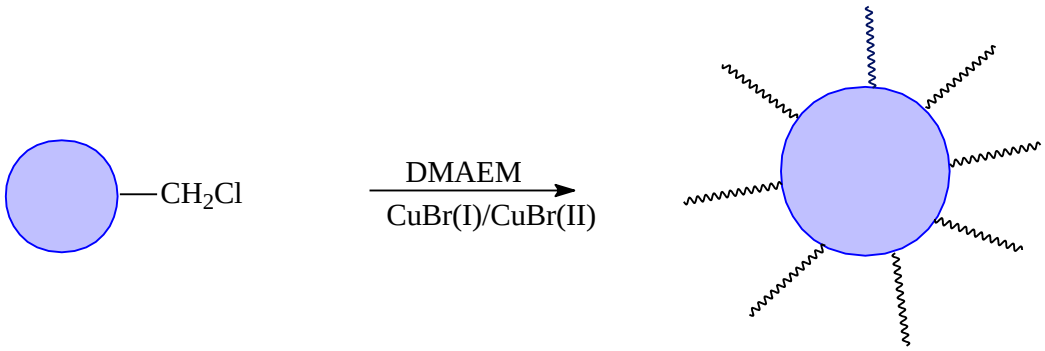


Figure 4.4 : Schematic demonstration of core-shell structure.

The grafting percentage (GP) was determined by calculating the percentage increase in weight by using following equation:

$$GP = \left[\frac{(m_{gf} - m_0)}{m_0} \right] 100\% \qquad \textbf{(4.1)}$$

where, m_0 and m_{gf} are the weights of the beads before and after grafting, respectively and grafting degree was found as 46 % for 18 h.

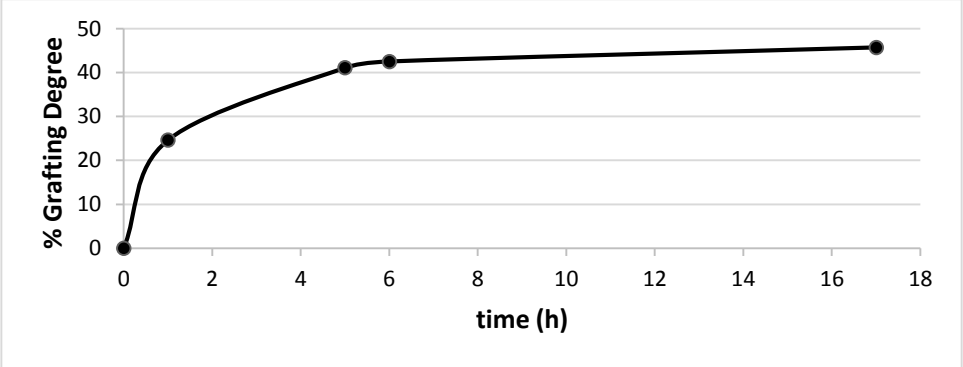


Figure 4.5 : Conversion of the graft copolymerization of 2-(dimethylamino) ethyl methacrylate onto PVBC at 60 ^{0}C.

Figure 4.5 represents the conversion of graft copolymerization of 2-(dimethylamino) ethyl methacrylate onto PVBC in the presence of Cu (I)/Cu (II) and PMDETA at 60^0 C. The plot indicates that the concentration of growing radicals is constant during the polymerization.

The resins were characterized by using FT-IR spectrocopy. According to the Fig 4.6.a, PVBC-EGDMA resin showed a sharp band 1720 cm−1 corresponding to the ester carbonyl group of the crosslinking agent. Also, resin showed characteristic C-Cl stretching at about 698 cm−1. The C–N stretching vibration of tertiary amine in 2-(dimethylamino) ethyl methacrylate is observed as medium or weak bands in the region 1250-1020 cm-1 (Fig.4.6 b and 4.6 c). C-Cl stretching at about 698 cm−1 in PVBC resin disappears after grafting reaction of poly (2-(dimethylamino) ethyl methacrylate). According to the Fig.4.6d, the peak at 3381 cm−1 become stronger after dye sorption of the resin.

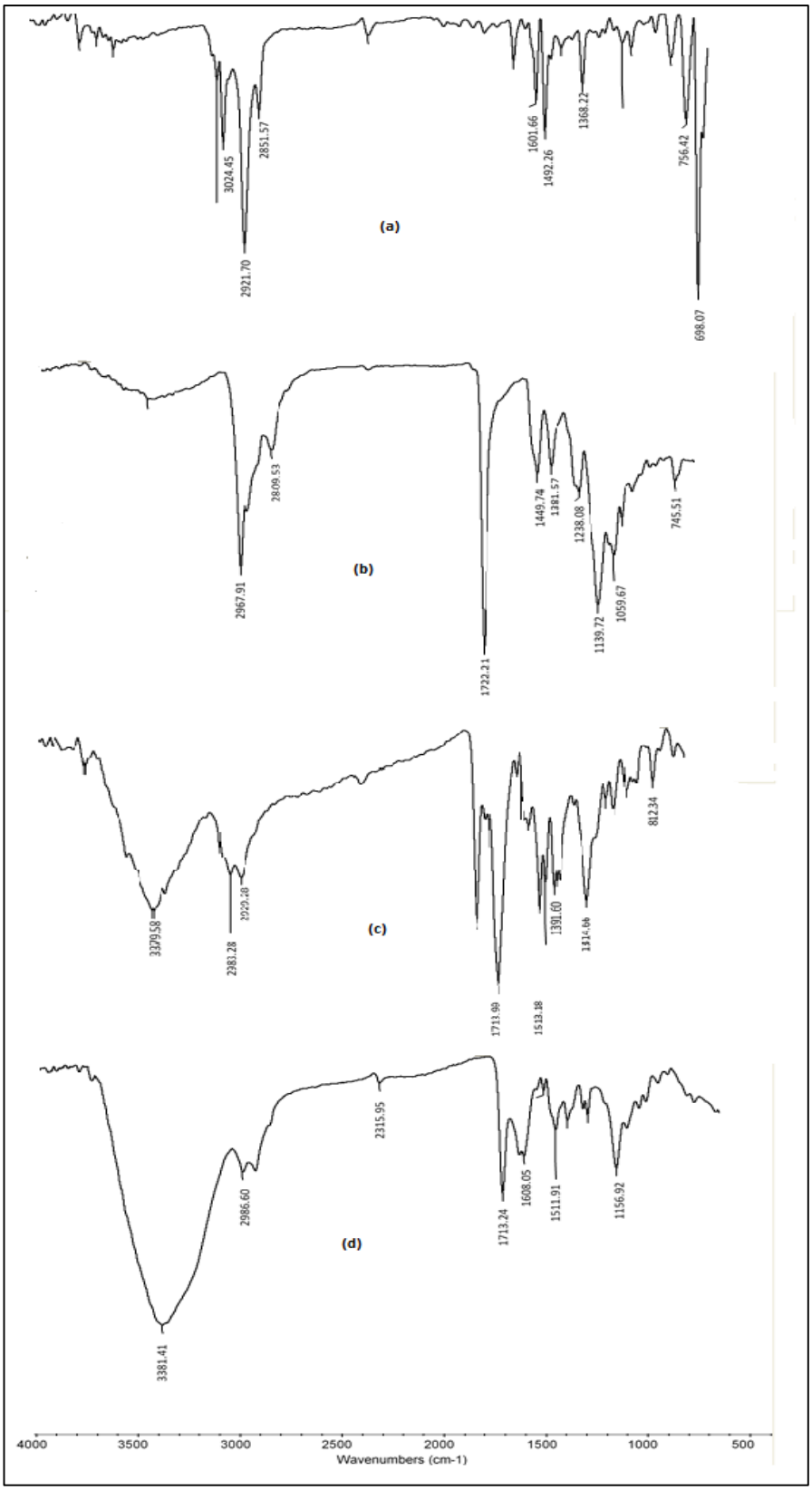
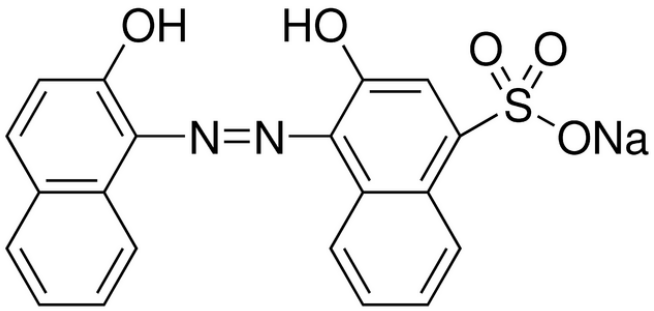


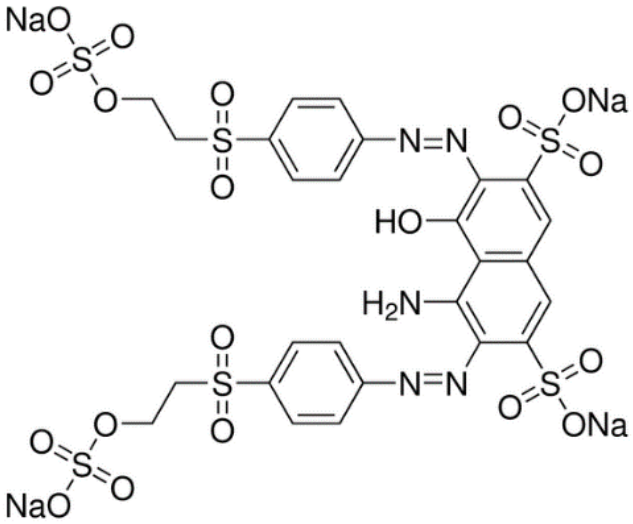
Figure 4.6 : FT-IR spectra of (a) PVBC (b) crosslinked sorbent (c) grafted core-shell (d) dye loaded core-shell.

4.4 Extraction of Dyes

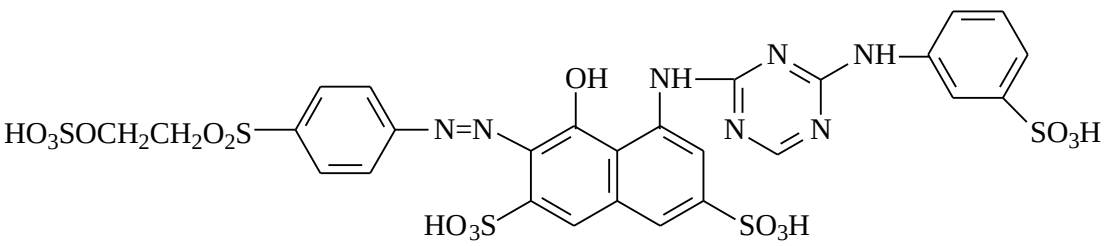
Dye extraction experiments were carried out simply by contacting wetted polymer samples with aqueous dye solutions at room temperature. Capacities were assigned by colorimetrical analysis of residual dye contents. Calcon, Reactive Red and Everzol Black were used as acidic dyes for determining of the resin capacity and kinetic studies (Figure 4.7).



Calcon



Everzol Black

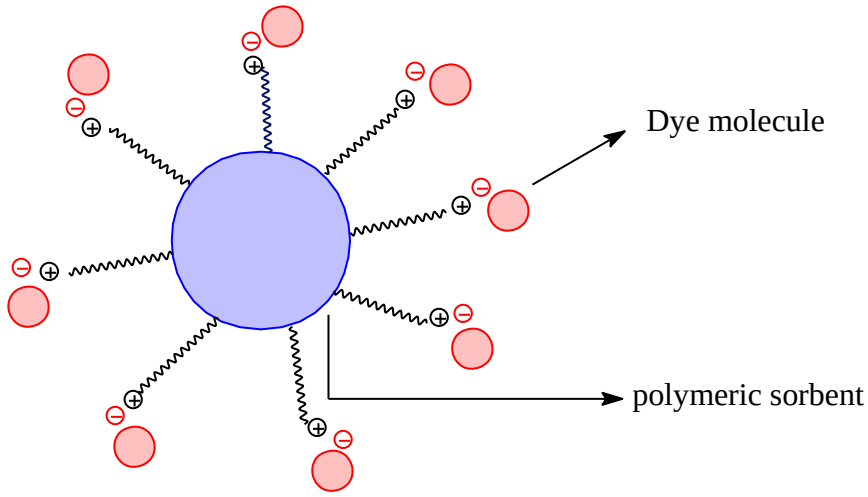


Reactive Red

Figure 4.7 : Acidic Dyes.

It has been reported that the basic mechanism in dyeing protein fibers with acid dyes is salt formation with amino groups as follows [105]:

$^{+}NH_3 + {}^{-}Dye \longrightarrow NH_3Dye$ **(a)**



(b)

Figure 4.8 : (a) Salt formation of dyes with amino groups (b) Salt formation.

According to the Table 4.1, Dye sorption capacities of the resin 2 higher than resin 1. Because core-shell structure of the Resin 2 supplies homogenous reaction condition.

Table 4.1: Maximum Dye Sorption Capacities of the Resin 1 and Resin 2.

Dyes	**Capacity (g dye/g resin)**		**λ_{max} (nm)**
	DMAEM resin (resin 1)	**DMAEM-g-PVBC resin (resin 2)**	
Calcon	0.37	0.66	552
Everzol Black	0.27	0.98	597
Reactive Red	0.57	0.90	591

The solution pH is an important parameter in the adsorption process because it can affect the interaction of the surface functional groups of the adsorbate and the adsorbent. In addition, the properties of the activated carbon and of the dyes may indicate whether adsorption is favorable in acid or basic solutions [106].

Table 4.2: Maximum dye sorption capacities of Resin 1 and Resin 2 depending on pH.

Dyes	pH	Capacity (g dye/ g resin)	
		Resin 1	Resin 2
Reactive Red	2	0.20	0.49
	4	0.34	0.44
	6	0.37	0.45
	8	0.35	0.38
Everzol Black	2	0.32	0.45
	4	0.35	0.50
	6	0.37	0.50
	8	0.38	0.10
Calcon	2	0.27	0.40
	8	0.20	0.30

The sorption capacity of the resin does not change very much in lower pH (Table 4.2). The explanation for this is that under acidic conditions hydrogen atoms (H^+) in the solution could protonate the amine group and thus cause an increase in pH [107,108]. Sorption capacity of the sorbents were studied depending on the different dye concentration. Sorption capacities of the resins increase depending on higher dye concentration (Table 4.3).

Table 4.3: Maximum dye sorption capacity of the Resin 1 and Resin 2 depending on different concentrations.

Dyes	Concentration (g dye/L)	Capacity (g dye/g resin)	
		Resin 1	Resin 2
Calcon	0.80 g dye /L	0.32	0.66
	0.40 g dye/L	0.21	0.37
	0.16 g dye/L	0.15	0.24
Everzol Black	0.80 g dye/L	0.37	0.98
	0.40 g dye/L	0.27	0.60
	0.16 g dye/L	0.19	0.37
Reactive Red	0.80 g dye /L	0.57	0.90
	0.40 g dye/L	0.32	0.64
	0.16 g dye/L	0.13	0.22

Dye sorption capacities of the resin was investigated depending on different ionic stregth (Table 4.4). NaCl was used for this purpose. Dye sorption capacities did ot

change against to ionic strength. This property is very important. The resin is used in ionic medium.

Table 4.4: Maximum dye sorption capacities of the core-shell depending on NaCl.

Dyes	NaCl M (mol/L)	Capacity (g dye/ g resin)
Calcon	0.02	0.21
	0.03	0.18
Everzol Black	0.02	0.20
	0.03	0.18
Reactive Red	0.02	0.12
	0.03	0.14

4.5 Dye Sorption Kinetic of the Sorbent

This material is able to remove the acidic dyes completely even from highly diluted aqueous dye solutions which are highly important. We performed batch kinetic sorption experiments with highly diluted dye solutions (0.0001 g dye / L water) to investigate the efficiency of the sorbent in the presence of trace quantities of dyes. The concentration–time plot in Figure 4.9 shows that within about 60 min of contact time, the dye concentration falls to zero for all dyes.

Adsorption dynamics is useful to describe the rate of solute adsorption, which controls the residence time of uptake of the adsorbate at the solid–solution interface. Three kinetic models were used to analyze adsorption kinetics at different initial dye concentrations, namely, pseudo-first-order, pseudo-second-order, and intra-particle diffusion models. The Lagergren first-order rate equation is one of the most widely used equations for the sorption of solute from a liquid solution [109]. For this model, the following relation was used for the variation of adsorbed concentration with respect to time.

$$\log (q_{eq}/q_{eq} - q_t) = (k_1 . t) / 2.303 \qquad \textbf{(4.2)}$$

where k_1 is the rate constant of pseudo-first-order adsorption (min^{-1}) and q_{eq} and q_t denote the amounts of adsorption ($mg.g^{-1}$) at equilibrium and at time t, respectively. The slopes and intercepts of plots of log ($q_{eq} - q_t$) versus t were used to determine the pseudo-first-order rate constant k_1 and q_{eq}.

The kinetics of sorption are an important aspect of the process control of removal of pollutants. The linear form of the equation describing the adsorption kinetics by the pseudo-second-order model is as follows:

$$t/q_t = 1/k_2 q_e^{\ 2} + 1/q_{et} \qquad \textbf{(4.3)}$$

The rate parameters k_2 and q_e can be directly obtained from the intercept and slope of the plot of t/q_t versus t (Fig. 4.10). If pseudo-second-order kinetics is applicable, the plot gives a linear relationship which allows computation of k_2 (Fig.4.11).

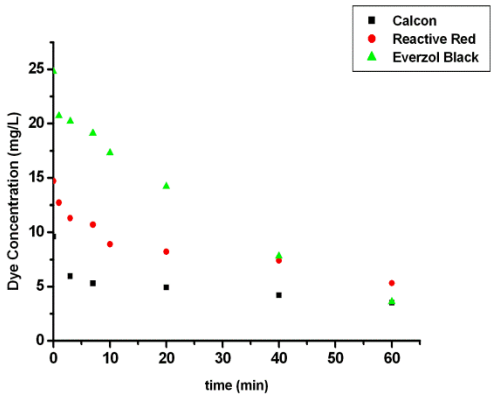


Figure 4.9 : Dye loading capacity – time plots for Resin 2.

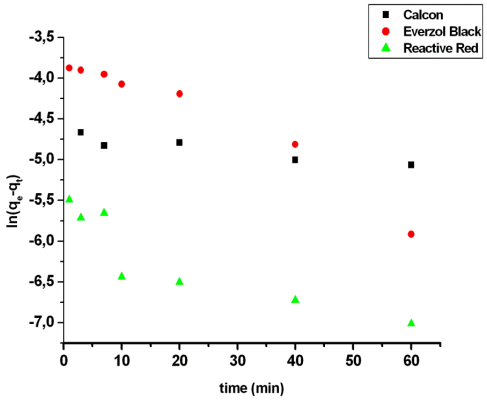


Figure 4.10 : Pseudo-first-order model plot for the Resin 2.

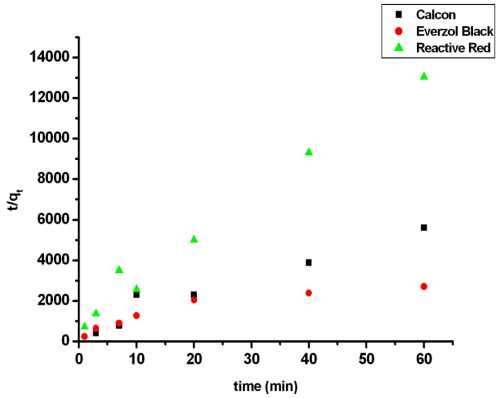


Figure 4.11 : Pseudo-second-order model plot for the Resin 2.

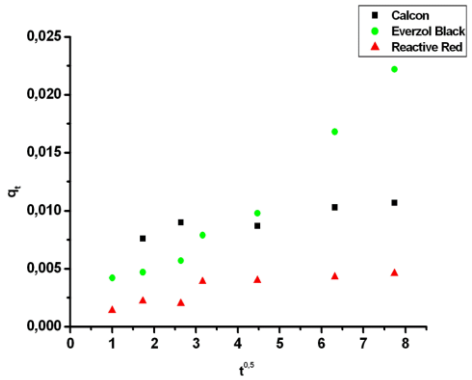


Figure 4.12 : Intra-particular diffusion plots for Resin 2.

The intraparticle diffusion equation is given as [110]:

$$q_t = K_p \times t^{0.5} + C \qquad \textbf{(4.4)}$$

Where K_p (mg/g.min$^{0.5}$) is the intraparticle diffusion rate constant and C is the intercept. The boundary layer thickness is described by the values of the intercept.

Table 4.5: Pseudo-first-order, second-order and intra-particular diffusion kinetics models for adsorption of dyes for Resin 2.

	First Order				Second Order			Intra-particular Diffusion	
Dyes	q_{eq},exp (mg.g^{-1})	$k_1 \times 10^{-2}$ (min^{-1})	q_e (mg.g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg.g^{-1})	R^2	K_i (mm.g^{-1} min$^{-0.5}$)	R^2
C	0.0170	0.64	0.009	0.8723	0.403	0.011	0.9953	0.0005	0.8669
RB	0.0249	3.3	0.024	0.9538	0.059	0.0254	0.8565	0.0027	0.9601
RR	0.0055	2.38	0.0032	0.7809	0.211	0.0049	0.9859	0.0005	0.7891
*C: Calcon; EB: Everzol Black; RR: Reactive Red									

As seen in Table 4.5, the correlation coefficients R^2 of resin 2 for the pseudo-second-order kinetic model are 0.9953 for Calcon and 0.9859 for Reactive Red, respectively and their calculated q_e values agree with the experimental q_e values. This confirms that the adsorption data are well represented by the pseudo-second-order kinetic model. From Table 4.5, it was observed that the intraparticle diffusion model is suitable for Everzol black.

Also, crosslinked polymers kinetics were studied.

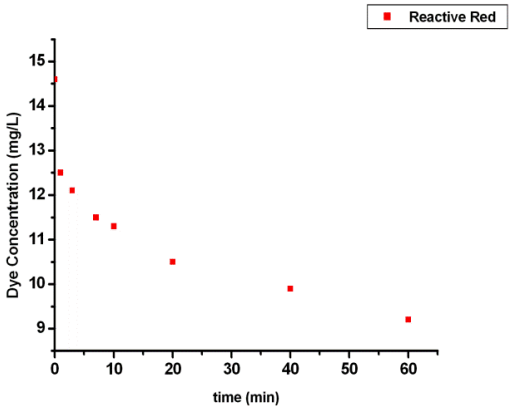


Figure 4.13 : Dye loading capacity – time plots for Resin 1.

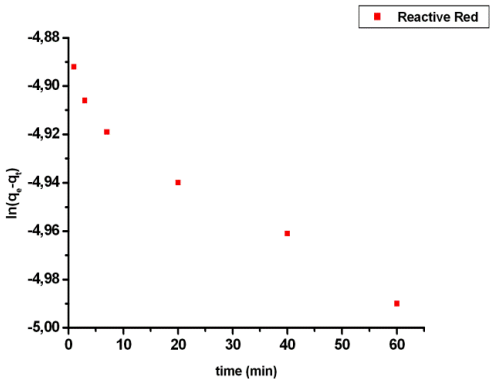


Figure 4.14 : Pseudo-first-order model plot for the Resin 1.

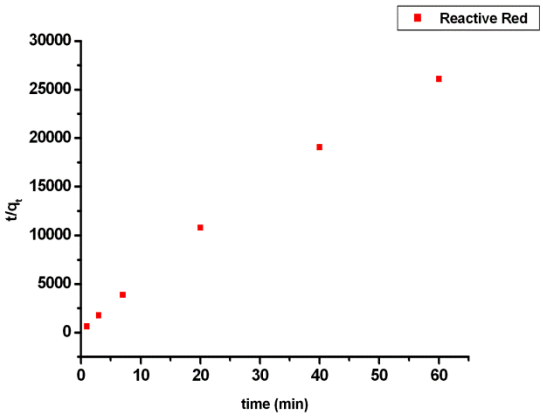


Figure 4.15 : Pseudo-second-order model plot for Resin 1.

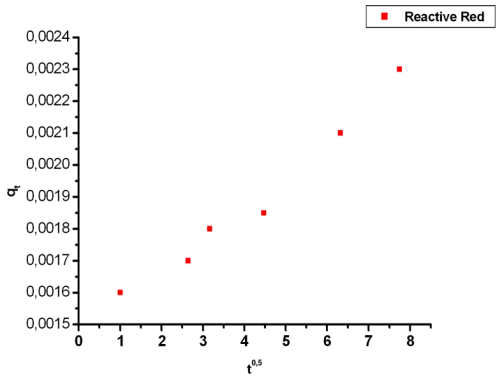


Figure 4.16 : Intra-particular diffusion plots Resin 1.

As seen in Table 4.6, the correlation coefficients R^2 of resin 2 for the pseudo-second-order kinetic model is 0.9933 for Reactive Red, respectively and their calculated q_e values agree with the experimental q_e values. This confirms that the adsorption data are well represented by the pseudo-second-order kinetic model.

Table 4.6: Pseudo-first-order, second-order and intra-particular diffusion kinetik models for adsorption of Reactive Red on the Resin 1.

First Order					Second Order			Intra-particular Diffusion	
Dye	$q_{eq,exp}$ ($mg.g^{-1}$)	k_1 (min^{-1})	q_e ($mg.g^{-1}$)	R^2	k_2 (g mg^{-1} min^{-1})	q_e ($mg.g^{-1}$)	R^2	K_i ($mm.g^{-1}$ $min^{-0.5}$)	R^2
Reactive Red	0.003	0.001	0.0074	0.963	0.5	0.0023	0.993	0.0001	0.963

5. CONCLUSION

Two types of new sorbents are compared crosslinked DMAEM resin and their core-shell structure. Resins were characterized by using FT-IR spectroscopy and analytical techniques. These resins were used to remove acidic dyes from water. Dye sorption experiments were carried out depending on pH and ionic strength. The resins could be used wide range of pH. According to experimental results, capacity of the core-shell type resin has higher then DMAEM resin. Also, increasing ionic strenght dye sorption capacity does not change dramatically. Also, kinetic parameters of the resin were obtained by using kinetic model described in the literature.

The resins could be regenerated by using KOH solution (H_2O %50- ethanol %50). Regeneration of the resins could be performed successfully and regenaration capacity was found as about for reactive red 0.83 g dye /g resin.

These resins could be used to remove acidic dyes without using their properties and capacities.

REFERENCES

[1] **Ju Kim J., Park K.** (2002). Smart Polymers for Bioseparation and Bioprocessing. 29 West 35th Street, New York, NY 10001.

[2] **Chanda M, Salil K. Roy. (**2008). Industrial Polymers, Specialty Polymers, and Their Applications, *Taylor & Francis Group* 6000 Broken Sound Parkway NW, Suite 300 Boca Raton, FL 33487-2742.

[3] **Kaşgöz, H.** (2006). New sorbent hydrogels for removal of acidic dyes and metal ions from aqueous solutions. *Polymer Bulletin* 56, 517–528.

[4] **Billmeyer, F.W.** (1984). Textbook Polym. Sci., *3rd Edition, John Wiley&Sons.*

[5] **Braun, D., Cherdonron, H., Kern, W.** (1984). Practical Macromolecular Organic Chem., *Harwood Academic Publisher.*

[6] **Dowding, P.J., Vincent, B.** (2000). *Colloids and Surfaces*, 161-259.

[7] **Senkal, B. F.** (2001). Synthesis and Characterization of Macromolecules.

[8] **Wang J.S., Matyjaszewski K.** (1995). Controlled living radical polymerization–atom-transfer radical polymerization in the presence of transition-metal complexes. *J Am Chem Soc*, 117, 5614–5.

[9] **Matyjaszewski K., Xia J.H.** (2001). Atom transfer radical polymerization. *Chem Rev*, 101, 2921–90.

[10] **Braunecker W.A., Matyjaszewski K.** (2007). Controlled/living radical polymerization: features, developments, and perspectives. *Prog Polym Sci*, 32, 93–146.

[11] **Matyjaszewski K., Tsarevsky N.** (2009). Nanostructured functional materials prepared by atom transfer radical polymerization. *Nat Chem*, 1, 276–88.

[12] **Lena F., Matyjaszewski K.** (2010). Transition metal catalysts for controlled radical polymerization. *Prog Polym Sci,* 35, 959– 1021.

[13] **Coessens V., Pintauer T., Matyjaszewski K.** (2001). Functional polymers by atom transfer radical polymerization. *Prog Polym Sci*, 26, 337–77.

[14] **Pyun J., Matyjaszewski K.** (2001). Synthesis of nanocomposite organic/inorganic hybrid materials using controlled/"living"radical polymerization. *Chem Mater*, 13, 3436–48.

[15] **Kato M., Kamigaito M., Sawamoto M., Higashimura T.** (1995). Polymerization of methyl methacrylate with the carbon tetrachloride/dichlorotris-(triphenylphosphine)ruthenium(II)/methylaluminum bis(2,6-di-tert-butylphenoxide) initiating system: possibility of living radical polymerization. *Macromolecules,* 28, 1721–3.

[16] **Matyjaszewski K.** (1999). Transition metal catalysis in controlled radical polymerization: atom transfer radical polymerization. *Chem Eur J*, 5, 3095–102.

[17] **Sawamoto M., Kamigaito M.** (1996). Living radical polymerization based on transition metal complexes. *Trends Polym Sci*, 4, 371–7.

[18] **Kamigaito M., Ando T., Sawamoto M.** 2001. Metal-catalyzed living radical polymerization. *Chem Rev*, 101, 3689–745.

[19] **Goto A, Fukuda T.** (2004). Kinetics of living radical polymerization. *Prog Polym Sci*, 29, 329–85.

[20] **Matyjaszewski K., Davis T.P.** (2002). Handbook of radical polymerization. *Hoboken: Wiley-Interscience;* p. 936.

[21] **Matyjaszewski K, Tsarevsky NV, Braunecker WA, Dong H, Huang J, Jakubowski W, Kwak Y, Nicolay R, Tang W, Yoon JA.** (2007). Role of Cu-0 in controlled/"living" radical polymerization. *Macromolecules*, 40, 7795–806.

[22] **Lin C.Y., Coote M.L., Gennaro A., Matyjaszewski K.** (2008). Ab initio evaluation of the thermodynamic and electrochemical properties of alkyl halides and radicals and their mechanistic implications for Atom Transfer Radical Polymerization. *J Am Chem Soc*, 130, 12762–74.

[23] **Tsarevsky N.V., Matyjaszewski K.** (2007). "Green" Atom Transfer Radical Polymerization: from process design to preparation of welldefined environmentally friendly polymeric materials. *Chem Rev*, 107, 2270–99.

[24] **Wang Y., Matyjaszewski K.** (2010). ATRP of MMA in polar solvents catalyzed by FeBr2 without additional ligand. *Macromolecules*, 43, 4003–5.

[25] **Wang Y., Matyjaszewski K.** (2011). ATRP of MMA catalyzed by (FeBr2)-Br-II in the presence of triflate anions. *Macromolecules*, 44, 1226–8.

[26] **Wang Y, Zhang Y., Parker B., Matyjaszewski K.** (2011). ATRP of MMA with ppm levels of iron catalyst. *Macromolecules*, 44, 4022–5.

[27] **Wang J.S., Matyjaszewski K.** (1995). *Macromolecules*, 28, 7572–7573.

[28] **Vandevivere, P.C., Bianchi, R., Verstraete, W. (**1998**).** Treatment and reuse of wastewater from the textile wet-processing industry: review of emerging technologies. *J. Chem. Technol. Biotechnol*, 72, 289–302.

[29] **Sun, Q., Yang, L. (**2003**).** The adsorption of basic dyes from aqueous solution on modified peat-resin particle. *Water Res.*, 37, 1535–1544.

[30] **Ravi Kumar R, M.N.V., Sridhari, T.R., Bhavani, K.D., Dutta, P.K. (**1998**).** Trends in color removal from textile mill effluents, *Colorage*, 40, 25–34.

[31] **Ghoreishi, S.M., Haghighi, R. (**2003**).** Chemical catalytic reaction and biological oxidation for treatment of non-biodegradable textile effluent. *Chem. Eng. J,*. 95, 163–169.

[32] **Jain, A.K., Gupta, V.K., Bhatnagar, A., Suhas. (**2003**).** Utilization of industrial waste products as adsorbents for the removal of dyes. *J. Hazardous Mater,* B 101, 31–42.

[33] **Ho, Y.S., McKay, G. (**2003**).** Sorption of dyes and copper ions onto biosorbents. *Process Biochem,* 38, 1047–1061.

[34] **Derbyshire, F., Jagtoyen, M., Andrews, R., Rao, A., Martin-Gullon, I., Grulke, E.** (2001)**.** Carbon materials in environmental applications. In: Radovic, L.R. (Ed.), *Chemistry and Physics of Carbon,* Vol. 27. Marcel Dekker, New York, pp. 1–66.

[35] **Pereira, M.F.R., Soares, S.F., Orfao, J.J.M., Figueiredo, J.L. (**2003) Adsorption of dyes on activated carbons: Influence of surface chemical groups. *Carbon,* 41, 811–821.

[36] **Marco, A., Esplugas, S., Saum, G. (**1997) How and why to combine chemical and biological processes for wastewater treatment. *Water Sci. Technol,* 35, 231–327.

[37] **Bhattacharyya, K.G., Sarma, A. (**2003)**.** Adsorption characteristics of the dye, Brilliant Green, on Neem leaf powder. *Dyes Pigments,* 57, 211–222.

[38] **Ramakrishna, K.R., Viraraghavan, T. (**1997). Dye removal using low cost adsorbents. *Water Sci. Technol,* 36, 189–196.

[39] **Streat, M., Patrick, J.W., Pe´rez, M.J. (**1995)**.** Sorption of phenol and para-chlorophenol from water using conventional and novel activated carbons. *Water Res*., 29, 467–472.

[40] **Bailey, S.E., Olin, T.J., Bricka, M., Adrian, D.D. (**1999)**.** A review of potentially low-cost sorbents for heavy metals. *Water Res.,* 33, 2469–2479.

[41] **Rozada, F., Calvo, L.F., Garcia, A.I., Martin-Villacorta, J., Otero, M., (**2003)**.** Dye adsorption by sewage sludge-based activated carbons in batch and fixed-bed systems. *Bioresour. Technol,* 87, 221–230.

[42] **Carrasco-Marin, F., Alvarez-Merino, M.A., Moreno-Castilla, C. (**1996)**.** Microporous activated carbons from a bituminous coal. *Fuel,* 75, 966–970.

[43] **Karaca, S., Gurses, A., Bayrak, R. (**2004)**.** Effect of some pretreatments on the adsorption of methylene blue by Balkaya lignite. *Energy Convers. Manage***,** 45, 1693–1704.

[44] **Valix, M., Cheung, W.H., McKay, G. (**2004) Preparation of activated carbon using low temperature carbonisation and physical activation of high ash raw bagasse for acid dye adsorption. *Chemosphere,* 56, 493–501.

[45] **Shichi, T., Takagi, K. (**2000). Clay minerals as photochemical reaction fields. *J. Photochem. Photobiol. C: Photochem. Rev.,* 1, 113–130.

[46] **Alkan, M., Demirbas, O., Celikcapa, S., Dogan, M. (**2004). Sorption of acid red 57 from aqueous solutions onto sepiolite. *J. Hazardous Mater,* 116, 135–145.

[47] **Krysztafkiewicz, A., Binkowski, S., Jesionowski, T. (**2002)**.** Adsorption of dyes on a silica surface. *Appl. Surf. Sci.,* 199, 31–39.

[48] **Armagan, B., Turan, M., Celik, M.S. (**2004). Equilibrium studies on the adsorption of reactive azo dyes into zeolite. *Desalination,* 170, 33–39.

[49] **Meshko, V., Markovska, L., Mincheva, M., Rodrigues, A.E. (**2001)**.** Adsorption of basic dyes on granular activated carbon and natural zeolite. *Water Res.,* 35, 3357–3366.

[50] **Calzaferri, G., Bruhwiler, D., Megelski, S., Pfenniger, M., Pauchard, M., Hennessy, B., Maas, H., Devaux, A., Graf, A. (**2000)**.** Playing with dye molecules at the inner and outer surface of zeolite. *L. Solid States Sci.,* 2, 421–447.

[51] **Karcher, S., Kornmuller, A., Jekel, M. (**2001)**.** Screening of commercial sorbents for the removal of reactive dyes. *Dyes Pigments*, 51, 111–125.

[52] **Takemoto, K.** (1997). *Functional Monomers and Polymers*.

[53] **Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H.** (2001). *Chem Rev*, 101, 3747–3792.

[54] **Hadjichristidis, N.; Iatrou, H.; Pitsikalis, M.** (2006). Mays. *J. Prog Polym Sci*, 31, 1068–1132.

[55] **Zhang, M.; Mu¨ller, A. H. E.** (2005). *J. Polym. Sci., Part A: Polym. Chem., 43*, 3461.

[56] **Sheiko, S. S.; Sumerlin, B. S.; Matyjaszewski, K.** (2008). *Prog. Polym. Sci., 33*, 759.

[57] **Iha R. K., Wooley K. L., Nyström A. M., Burke D. J., Kade M. J., and Hawker C. J.** (2009). *Chem Rev.,* 109, 5620-5686.

[58] **Zhang, M.; Breiner, T.; Mori, H.; Mu¨ller, A. H. E.** (2003). *Polymer, 44*, 1449.

[59] **Pokhrel, D., Viraraghavan, T. (**2004). Treatment of pulp and paper mill wastewater — a review. *Sci. Total Environ*, 333, 37–58.

[60] **Slokar, Y.M., Majcen Le Marechal, A. (**1998). Methods of decoloration of textile wastewaters. *Dyes Pigments* 37, 335–356.

[61] **Dele´e, W., O'Neill, C., Hawkes, F.R., Pinheiro, H.M. (**1998)**.** Anaerobic treatment of textile effluents: A review. *J. Chem. Technol. Biotechnol.* 73, 323–335.

[62] **Cooper, P. (**1993)**.** Removing color from dyehouse waste waters: A critical review of technology available. *J. Soc. Dyers Colorists,* 109, 97–100.

[63] **Aksu, Z. (**2005)**.** Application of biosorption for the removal of organic pollutants: A review. *Proc. Biochem.* 40, 997–1026.

[64] **Wesenberg, D., Kyriakides, I., Agathos, S.N.,** (2003)**.** White-rot fungi and their enzymes for the treatment of industrial dye effluents. *Biotechnol. Adv.,* 22, 161–187.

[65] **Fu, Y., Viraraghavan, T. (**2001)**.** Fungal decolorization of dye wastewaters: A review. *Bioresour. Technol.,* 79, 251–262.

[66] **Stolz, A.** (2001)**.** Basic and applied aspects in the microbial degradation of azo dyes. *Appl. Microbiol. Biotechnol.*, 56, 69–80.

[67] **Dabrowski, A.** (2001)**.** Adsorption, from theory to practice. *Adv. Colloid Int. Sci.,* 93, 135–224.

[68] **Inglezakis, V., Paulopoulos, S.** Adsorption, Ion Exchange and Cataylsis Design of Operations and Enviromental Applications. 31-56.

[69] **Babel, S., Kurniawan, T.A.** (2003). Low-cost adsorbents for heavy metals uptake from contaminated water: A review. *J. Hazardous Mater.* B, 97, 219–243.

[70] **Alkan, M., Celikcapa, S., Demirbas, O, Dogan, M.** (2005). Removal of reactive blue 221 and acid blue 62 anionic dyes from aqueous solutions by sepiolite. *Dyes Pigments,* 65, 251–259.

[71] **Gurses, A., Karaca, S., Dogar, C., Bayrak, R., Acikyildiz, M., Yalcin, M.** (2004). Determination of adsorptive properties of clay/water system: Methylene blue sorption. *J. Colloid Int. Sci.*, 269, 310–314.

[72] **Wang, C.C., Juang, L.C., Hsu, T.C., Lee, C.K., Lee, J.F., Huang, F.C.** (2004)**.** Adsorption of basic dyes onto montmorillonite. *J. Colloid Int. Sci.,* 273, 80–86.

[73] **Al-Bastaki, N., Banat, F.** (2004)**.** Combining ultrafiltration and adsorption on bentonite in a one-step process for the treatment of colored waters. *Resour. Conser. Recycl.*, 41, 103–113.

[74] **Ozcan, A.S., Erdem, B., Ozcan, A.** (2004)**.** Adsorption of acid blue 193 from aqueous solutions onto Na-bentonite and DTMA-bentonite. *J. Colloid Int. Sci.*, 280, 44–54.

[75] **Ozdemir, O., Armagan, B., Turan, M., Celik, M.S.** (2004)**.** Comparison of the adsorption characteristics of azo-reactive dyes on mezoporous minerals. *Dyes Pigments*, 62, 49–60.

[76] **Al-Ghouti, M.A., Khraisheh, M.A.M., Allen, S.J., Ahmad, M.N.** (2003)**.** The removal of dyes from textile wastewater: A study of the physical characteristics and adsorption mechanisms of diatomaceous earth. *J. Environ. Manage.*, 69, 229–238

[77] **Atun, G., Hisarli, G., Sheldrick, W.S., Muhler, M.** (2003). Adsorptive removal of methylene blue from colored effluents on Fuller_s earth. *J. Colloid Int. Sci.* 261, 32–39.

[78] **Espantaleon, A.G., Nieto, J.A., Fernandez, M., Marsal, A.** (2003). Use of activated clays in the removal of dyes and surfactants from tannery waste waters. *Appl. Clay Sci.*, 24, 105–110.

[79] **Orthman, J., Zhu, H.Y., Lu, G.Q.** (2003). Use of anion clay hydrotalcite to remove coloured organics from aqueous solutions. *Sep. Purif. Technol.,* 31, 53–59.

[80] **Lazaridis, N.K., Karapantsios, T.D., Geogantas, D.** (2003). Kinetic analysis for the removal of a reactive dye from aqueous solution onto hydrotalcite by adsorption. *Water Res.,* 37, 3023–303

[81] **Shawabkeh, R.A., Tutunji, M.F.** (2003)**.** Experimental study and modelling of basic dye sorption by diatomaceous clay. *Appl. Clay Sci.*, 24, 111–120.

[82] **Crini, G., Morcellet, M.** (2002)**.** Synthesis and applications of adsorbents containing cyclodextrins. *J. Sep. Sci.* 25, 1–25.

[83] **Woolard, C.D., Strong, J., Erasmus, C.R.** (2002)**.** Evaluation of the use of modified coal ash as a potential sorbent for organic waste streams. *Appl. Geochem.*, 17, 1159–1164.

[84] **Phan, T.N.T., Bacquet, M., Morcellet, M.** (2000). Synthesis and characterization of silica gels functionalized with monochlorotriazinyl beta-cyclodextrin and their sorption capacities towards organic compounds. *J. Inclusion Phenom. Macrocyclic Chem.*, 38, 345–359.

[85] **Ahmed, M.N., Ram, R.N.** (1992)**.** Removal of basic dye from wastewater using silica as adsorbent. *Environ. Pollut.*, 77, 79–86.

[86] **Ozacar, M., Sengil, A.I.** (2002)**.** Adsorption of acid dyes from aqueous solutions by calcined alunite and granular activated carbon. *Adsorption* 8, 301–308.

[87] **Ozacar, M., Sengil, A.I. (**2003)**.** Adsorption of reactive dyes on calcined alunite from aqueous solutions. *J. Hazardous Mater.*, B 98, 211–224.

[88] **Dill, H.G.** (2001)**.** The geology of aluminium phosphates and sulphates of the alunite group minerals: A review. *Earth Sci. Rev.*, 53, 35–93.

[89] **Walker, G.M., Hansen, L., Hanna, J.A., Allen, S.J.** (2003)**.** Kinetics of a reactive dye adsorption onto dolomitic sorbents. *Water Res.*, 37, 2081–2089.

[90] **Benkli, Y.E., Can, M.F., Turan, M., Celik, M.S.** (2005)**.** Modification of organo-zeolite surface for the removal of reactive azo dyes in fixed-bed reactors. *Water Res.*, 39, 487–493.

[91] **Allen, S.J., McKay, G., Porter, J.F.** (2004)**.** Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems. *J. Colloid Int. Sci.* 280, 322–333.

[92] **Ho, Y.S., McKay, G.,** (1998b)**.** Sorption of dye from aqueous solution by peat. *Chem. Eng. J.*, 70, 115–124.

[93] **Poots, V.J.P., McKay, G., Healy, J.J.** (1976)**.** The removal of acid dye from effluent using natural adsorbents—I. Peat. *Water Res.* 10, 1061–1066.

[94] **Couillard, D.** (1994)**.** The use of peat in wastewater treatment. *Water Res.*, 28, 1261–1274.

[95] **Smith, E.F., McCarthy, P., Yu, T.C., Mark Jr., H.B. (**1977)**.** Sulfuric acid treatment of peat for cation exchange. *Chem. Eng. J.*, 49, 633–638.

[96] **Brown, P.A., Gill, S.A., Allen, S.J.** (2000)**.** Metal removal from wastewater using peat. *Water Res.*, 34, 3907–3916.

[97] **Bustard, M., McMullan, G., McHale, A.P.** (1998)**.** Biosorption of textile dyes by biomass derived from Klyveromyces marxianus IMB3. *Bioprocess. Eng.* 19, 427–430.

[98] **Nigam, P., Banat, I.M., Singh, D., Marchant, R.** (1996)**.** Microbial process for the decolorization of textile effluent containing azo,diazo and reactive dyes. *Process. Biochem.,* 31, 435–442.

[99] **Swamy, J., Ramsay, J.A.** (1999)**.** The evaluation of white rot fungi in the decolorisation of textile dyes. *Enz. Microbiol. Technol.,* 24, 130–137.

[100] **Jinqi, L., Houtian, L.** (1992)**.** Degradation of azo dyes by algae. *Environ. Pollut.,* 75, 273–278.

[101] **Mou, D.G., Lim, K.K., Shen, H.P.** (1991)**.** Microbial agents for decolorization of dye wastewater. *Biotechnol. Adv.,* 9, 613–622.

[102] **Mittal, A.K., Gupta, S.K.** (1996)**.** Biosorption of cationic dyes by dead macro fungus Fomitopsis carnea: Batch studies. *Water Sci.Technol.,* 34, 81–87.

[103] **Yang, R.T.** (2003). Adsorbents: Fundamentals and Applications. *John Wiley & Sons: Hoboken, NJ.*

[104] **Thomas, W.J.; Crittenden, B.** (1998). Adsorption Technology & Design; Butterworth Heinemann. *Oxford*, 8–30.

[105] **Sza´raz I, Forsling W.** (2000). *Polymer*, 41, 4831.

[106] **Vargas A, Cazetta A, Martins A.** (2011). *Chemical Engineering Journal,* 174, p. 117-125

[107] **Wu F.C., Tseng R.L., Juang R.S.** (2001). *Water Res.,* 35, 613- 415.

[108] **Sakkayawong N., Thiravetyan P., Nakbanpote W.** (2001). *Adv. 416 Chitin Sci.* 5, 568.

[109] **Lagergren S.** (1898). Zur theorie der sogenannten adsorption gelöster stoffe. *Kungliga Svenska VetenskapsakademiensHandlingar*, 24, 1–39.

[110] **Weber, W. J., Morris, J. C.** (1963). Kinetics of adsorption on carbon from solution. *J. Sanitary Eng. Div. Proceed. Am. Soc. Civil Eng.,* 89, 31–59.

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Hamamcı M., Torunoglu Turan G., Şenkal B.F., Grafting of Poly (2-(dimethylamino) ethyl methacrylate) onto Crosslinked Poly(vinyl benzyl chloride) Resin for Removal of Acidic Dyes, *International Congress- 44th World Chemistry Congress,* August 11-16, 2013, İstanbul, Turkey.

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